

Physics 25L lab manual

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*This is a modified version of the original manual
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May 9, 2020

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5 Atomic spectra and the Rydberg constant

Abstract: In this lab you will observe the visible spectrum of Hydrogen and use it to measure the Rydberg constant. Then you will use the spectrum of an unknown source to determine its atomic content.

5.1 Pre-lab preparation

The quantum explanation for atomic structure was developed in the early 1900's, based largely on the evidence for quantized energy levels of atoms that was accumulated in the late 1800's through measurements of various atomic spectra. In 1885, Johann Balmer measured the visible spectrum of Hydrogen and found the wavelengths of light that were present were related according to

$$\frac{1}{\lambda} = R \left(\frac{1}{2^2} - \frac{1}{n^2} \right); \quad \text{for } n > 2. \quad (14)$$

The ultraviolet and infrared portions of the spectrum were later measured (by Lyman, Paschen, Brackett and Pfund) and found to fit into similar formulas but with integers other than 2 in the first term (and in the inequality). They all measured the same coefficient, R , called the Rydberg constant. The origin of this formula was eventually understood within the Bohr model of the atom. The light from Hydrogen consists of photons of energy $E = h\nu = hc/\lambda$ that are emitted by atoms transitioning between electronic states that have discrete (quantized) energies of $E_n = -hcR/n^2$, where n is a positive integer. (These energy levels are illustrated in Fig. 18.) This understanding allowed the Rydberg constant to be calculated as $R = me^4/8\epsilon_0 h^3 c$, whereas previously it had been only an empirically determined value.⁹

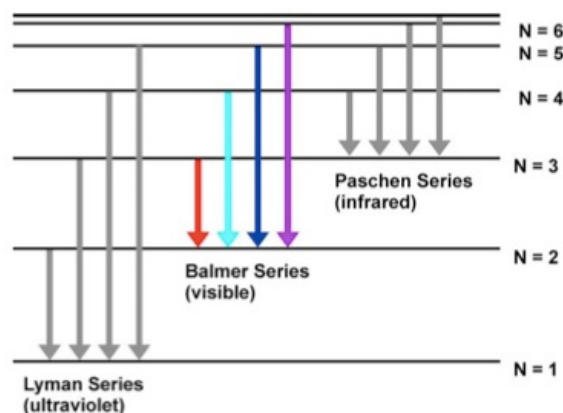


Figure 18: Diagram of the energy levels for a Hydrogen atom. Transitions between excited states down to the $n = 2$ state produce visible light (red to violet, left to right for the four lines shown) that you will observe in this lab. Transitions to the $n = 1$ state produce ultraviolet light, and those to the $n = 3$ state produce infrared light, neither of which can be seen by eye.

In this lab, you will measure the visible spectrum of Hydrogen as Balmer originally did and, from it, obtain a measurement of the Rydberg constant.

⁹Interestingly, the measured value of R did not match the prediction of the simplest Bohr model which uses $m = m_e$ because the electron and proton together lead to an effective “reduced mass”, m , that is very slightly below the electron mass. Furthermore, the spectrum of hydrogen was found to contain a set of wavelengths with a slightly different R value. These come from deuterium, which is hydrogen with a neutron in the nucleus, the mass of which further alters m). Both effects are smaller than 0.1% and only revealed by exquisitely precise measurements.

Equation (14) applies only to Hydrogen. Other atoms have a similar $1/n^2$ structure in their spectra but with a different coefficient. Each element's spectrum is uniquely characteristic, so spectra are often used to identify the elemental composition of a sample (or a star¹⁰!). After you have completed your measurements on a Hydrogen sample, you will measure the spectrum of an unknown sample (or two!) and identify its elemental composition.

5.1.1 Apparatus

The apparatus you'll use is called a *spectroscope*. It uses the phenomenon of interference, which you explored in the double slit experiment that you did two weeks ago, but instead of two slits, a spectroscope uses a *diffraction grating* with a very large number of equally spaced slits of identical width. Many equally spaced slits create a pattern with maxima at the same positions as in the pattern created by two slits with the same spacing, but when there are many slits, the maxima are much more narrowly peaked, (*i.e.*, the contrast is much improved). Because of its very large number of slits, a diffraction grating creates very sharp maxima.

The diffraction grating you will use is made by etching thin parallel lines on a piece of glass. Etched regions scatter light instead of transmitting it, so the non-etched regions between the etched lines act as slits. The etching process allows hundreds or thousands of lines per mm, so this type of diffraction grating has slits that are not only plentiful, but closely spaced as well. Your diffraction grating should specify the number of lines per mm, from which you can calculate the spacing, d , between any pair of slits.

The close spacing puts a large lever arm on the pattern (*i.e.* a greater angular separation between maxima) making it possible to distinguish maxima of many different wavelengths. As you'll recall, interference from slits separated by a distance d results in intensity maxima at angles θ for which $d \sin \theta = m\lambda$, where m is any positive integer. The $m = 0$ case is the central maximum with no deflection (*i.e.*, $\theta = 0$). By finding the θ values for the $m = \pm 1$ maxima for each of the different wavelengths, you can precisely determine those wavelengths. (You could also try to measure θ values for the $|m| > 1$ maxima, but as $|m|$ increases intensity is reduced, so you may not be able to see the $m = \pm 2$ maxima.)

A spectroscope allows precise measurement of these angles. The spectroscope you will be using consists of two cylinders that define the light path: one is a collimator; the other a telescope (Fig. 19a). The collimator has an opening at its far end that only admits light through a vertical slit. The width of the slit is narrow but adjustable. That slit shapes the light beam into a vertical line. Letting the light spread vertically doesn't degrade the resolution in θ because θ is an angle in the horizontal plane. Because a line allows more light to hit the detector (in this case, your eye) it is much easier to determine the location of a line than a point. The use of vertical slits in spectral measurements is so common that the observed maxima are called *spectral lines*.

The telescope part of the spectroscope allows you to scan through angles to find these lines and precisely measure their θ angle. The telescope has an adjustable eyepiece, to allow you to focus on the lines, and cross-hairs to help with visual alignment. The angular position of the telescope can be measured with scales situated on either side of the spectrometer. The scales measure degrees down to

¹⁰It is amusing to note how often dialogue in Star Trek episodes involves the captain asking for a "multi-spectral analysis" of some anomaly. Analyzing the spectrum of astrophysical objects is common, in fact so common that it would be done automatically, without the captain's specific request! But, it does provide tech-y sounding, and in this case not incorrect, dialogue.

one arc minute with Vernier markings.

Use of a Vernier scale takes a bit of explanation and some practice. There are some good extended descriptions online (e.g. [in Wikipedia](#)), so here we'll introduce it with a few examples specific to the scales you will be using. On the spectroscope, you will see a pair of scales that are arranged so that they slide past each other. The outer one has line markings for each half degree, while the inner one has markings corresponding to 0-30 arc minutes. The two scales are used together. Cartoons of two different measurements are shown in Fig. 20 to illustrate the procedure. First you look where the zero mark on the inner scale is located. In the left hand cartoon that is just past 210° ; in the right hand cartoon it is just past 229.5° . Then you look where the lines on the inner and outer scales align most closely. In the left hand cartoon that happens for the $15'$ mark; on the right side it happens at the $16'$ mark. These measure the number of arc minutes to add to the values obtained from the first step. So, the measurement on the left side is $210^\circ + 15' = 210^\circ + (15/60)^\circ = 210.250^\circ$, and the measurement on the right is $229.5^\circ + 16' = 229.5^\circ + (16/60)^\circ = 229.767^\circ$. To practice this yourself, figure out the measurement for the photo in the middle. Write your result in your logbook and, when you get to lab, compare it to what other students got.

The uncertainty in θ is driven by the one arc minute granularity of the scales, so it is appropriate to use $\delta\theta = 1'/\sqrt{12} = 0.3' = 0.005^\circ$. The scales thus provide rather precise angular measures, but it is possible to make mistakes in reading or calculating the values. There are a few things you can do to reduce the chance of such mistakes and their impact. First of all, you could have someone else (e.g. your lab partner) make the same reading (without telling them what you got) and compare. Secondly, the spectroscope has a scale on both sides, where the angles differ by 180° ; you should read and record both. If, after correcting for the 180° difference, you find that their values differ by more than the 0.005° precision of the scales, then there is an additional source of uncertainty. That could arise from things like warping of the scales, and it would then be the dominant uncertainty on your θ measurements. This approach of making multiple, independent measurements of the same quantity is always a good idea to help you validate your results.

It is also a good idea to record your raw readings in degrees and arc minutes, and then calculate the corresponding decimal degree values. This will help you disentangle any calculation errors that may occur. While the calculations in this case are not complicated, and the consequences of a mistake are small, this sort of fastidious data recording is a good habit to develop for your later research work, when both the chances and consequences of mistakes increase.

Finally, be aware that the scale measures an angular position on some arbitrary scale (i.e., the location of 0° is arbitrary). What you want to know in order to determine the wavelength using $d \sin \theta = \lambda$ is the angle *between* maxima. So you need to measure two angles and subtract, just like measuring a length requires two position measurements. You could do that by measuring the angular position of the central maximum, which we can call θ_0 , and the angular position of the $m = +1$ maximum, which we can call θ_{+1} . Then $\lambda = d \sin (\theta_{+1} - \theta_0)$. Similarly, you could measure the angular position of the $m = -1$ maximum and use $\lambda = d \sin (\theta_0 - \theta_{-1})$. If everything is perfectly aligned, $(\theta_{+1} - \theta_0) = (\theta_0 - \theta_{-1})$. If not, then neither value will be correct. You can cancel the effects of any mis-alignment by using *both* the $m = +1$ and $m = -1$ positions, i.e., $\lambda = d \sin (\theta_{+1} - \theta_{-1})/2$. Since you can't be certain that the diffraction grating is exactly perpendicular to the light path and the spectroscope's angular coordinate system, *you must use this difference of the two angles*. Finally, note that the direction in which the angles increase or decrease on the scale is arbitrary, so you should use the absolute value of the differences

$$\lambda = d \sin \left| \frac{\theta_{+1} - \theta_{-1}}{2} \right| \quad (15)$$

5.1.2 Safety and care of equipment

Be careful not to touch the glass part of the lamp, even when it's off. Not only might it be hot enough to burn you, but any oil from your fingertips that gets on the glass can absorb enough light energy to cause the glass to overheat and shorten the life of the lamp.

To help you discern the dim spectral lines, it is best to leave the room lights off. There is a desk lamp, but you should use it very sparingly. You can use the small flashlight provided when you need to read the angle scales. Reading the angle by taking a picture of the scale with a phone and then using the phone's digital zoom can help minimize errors in reading the Vernier. You will notice that there is considerable potential for parallax errors when reading the scales, either by eye or by phone. Think what you might do to minimize associated errors.

Keep in mind that the darkness and crowdedness of the room means you might back into or trip others who are trying to move around the lab (like your TA). In such situations it is a good idea to just move a bit more slowly.

The spectroscope has clamps to hold it in place while you measure angles. If you forget to release the clamps before trying to adjust the angle, you can damage the spectroscope. So, do not force any motion that doesn't feel smooth.

5.2 Getting started and gaining familiarity

Start with the Hydrogen discharge tube. There are two other tubes that contain other elements, which you will use next, but it's best to get familiar with the measurement on a simple spectrum like that of Hydrogen.

Play around with the spectroscope to make sure you understand how it works: align the telescope and collimator, and adjust the slit and crosshairs.

The grating should be approximately perpendicular to the light path. You can adjust it and lock its table in place. Any misalignment will skew the angles slightly, so as noted above, so you should measure the position of the spectral lines for both $m = +1$ and $m = -1$ and use half the difference to reduce the effect of any misalignment.

Look for each of the emission lines. You should see a total of four, although the last one, which is violet, is dim and difficult for some people to see. You can increase the slit width to make the lines easier to see, although you want to balance the need for visibility with the desire for narrow lines that can be measured more precisely. You may see a background of colors in addition to the main bright lines. This background can come either from stray light hitting the diffraction grating or from the ultraviolet light emitted by the hydrogen lamp exciting other atoms to emit. In fact, that is how fluorescent lights work. Ultraviolet emission produced by running a current through the gas in a long tube excites atoms in the white fluorescent material that coats the inside of the tube. That material then emits a large number of different wavelengths that we perceive as white light. You can use the hand held spectroscope (black trapezoidal object) provided to check out the spectrum of the fluorescent lights in the lab's ceiling.

5.3 Measuring the spectrum and extracting Rydberg's constant

Measure the angles for each of the spectral lines. (Remember to measure the position on both sides to correct for any misalignment of the grating, and to clamp the telescope before making a reading and then unclamp it before moving again.) If you are working with a lab partner, you should both take measurements independently. I suggest that one of you collect a full set of measurements and then the other collect another full set. You can each record readings for the other's dataset as a cross-check, but it is instructive to independently collect (*i.e.* align the cross-hairs) and analyze your own dataset. The writing in your logbook should make it clear who collected which data.

Once you have measured the angular positions of each of the emission lines, calculate their wavelengths and determine the uncertainty in the wavelengths. To find the uncertainty you will need to propagate the uncertainties in each of the measured angles, $\delta\theta_i$, to derive the uncertainty in λ using the standard error propagation approach described in Equation (5).

Then use Equation (14) to extract the Rydberg constant, R . This can be done in several ways, such as averaging all the measurements or fitting them. A fit is usually the best approach because it incorporates the uncertainties in each of the measurements, and the χ^2 of the fit provides a quantitative way to validate the measurements and uncertainties. So, fit your data.

Think about what would be the best functional form to use for the fit. It is not simple to solve Equation (14) for $\lambda(n)$, but you can calculate terms that are easy to plot. For example, a plot of $y = 1/\lambda$ versus $x = 1/2^2 - 1/n^2$ should be a line with a slope equal to R . Remember to propagate the uncertainties properly though! The uncertainty in $y = 1/\lambda$ must be derived from the uncertainty in λ using Equation (5).

If the χ^2 of your fit is too large or too small, it can indicate that your uncertainties are incorrectly estimated or that you made a mistake in calculating. The best way to figure this out is to make multiple measurements and compare them. If different measurements of the same quantity disagree completely then there is a mistake somewhere. (Note that recording the "color" of the lines you observe provides a coarse measurement of their wavelength, which you can use to validate that you have not made a major mistake in calculating λ from the measured angles). You can also compare your measured values from one set of data to the values from another set. They should agree to within the uncertainties that you have determined. If the disagreements are a bit larger than the uncertainties, you may have underestimated the uncertainties. Increasing the uncertainties on the λ 's to make the level of agreement between repeated measurements of them match a 68% confidence level will then make the uncertainty on the fitted R value more appropriately correspond to a 68% confidence level.

5.4 Measuring the spectrum of an unknown source

There are two other discharge tubes provided. They contain other elements. Replace the hydrogen tube with either one of these and measure its spectrum. You can remove the tubes by pushing them up and out of the black mounting box. The new ones should then slide in easily. Don't force it.

Compare your measured spectrum to the spectra given for standard sources in the following pages and determine the composition of the discharge tube. Note that, in some cases, the relative intensity of the different lines can be helpful, so it is wise to record a qualitative measure of that.

5.5 Going Beyond

There are several ways that exceptional students could go beyond the basics in this lab. A few ideas are listed below, but I encourage you to use your own creativity.

- Can you think of a way to quantitatively record the relative intensity of the emission lines?
- Can you use your measured value of the Rydberg constant, and Bohr's energy level calculation, to extract an upper or lower bound on the proton mass?
- Now that you understand how to use the spectroscope, can you use it to measure the spectrum of something else?

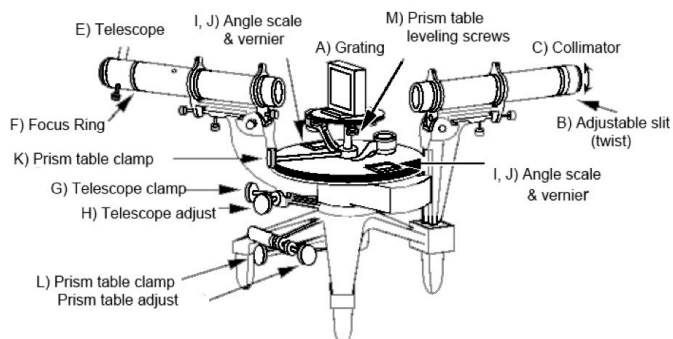


Figure 19: (a) Diagram of the spectroscope with its various components labelled. (b) Photo of the spectroscope. The light source is contained in the square black device behind it.

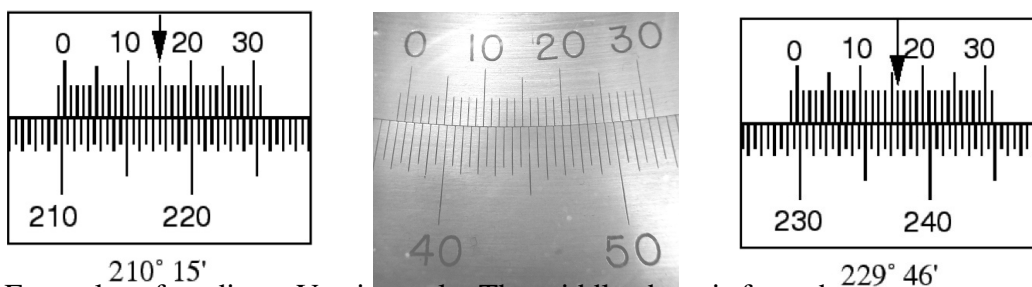


Figure 20: Examples of reading a Vernier scale. The middle photo is from the spectroscope that you will use. The left and right cartoons are discussed in the text to illustrate how to read the scale; the arrows in the cartoon show where the lines on the inner and outer scale are most closely aligned.