## The Hydrogen Balmer Series and Rydberg Constant

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#### **Objectives**

The objectives of this experiment are: (1) to study the emission of light from a hydrogen discharge source, (2) to learn the empirical formulas to characterize the pattern of spectral lines from hydrogen, (3) to learn the postulates for developing the Bohr model of the hydrogen atom, (4) to study and develop the Bohr theory of the hydrogen atom, (5) to measure the wavelengths of the Balmer series of visible emission lines from hydrogen, and (6) to learn to analyze the wavelength data to determine the Rydberg constant using the Bohr model formulation.

#### Theory

Hydrogen atoms in a discharge lamp emit a series of lines in the visible part of the spectrum. This series is called the Balmer Series after the Swiss teacher Johann Balmer (1825-1898) who, in 1885, found by trial and error a formula to describe the wavelengths of these lines. This formula is given by

$$\frac{1}{\lambda} = R \left[ \frac{1}{2^2} - \frac{1}{n^2} \right] \tag{1}$$

where n are integers, 3, 4, 5, ... up to infinity and R is a constant now called the Rydberg constant. In the SI system of units,  $R=1.097 \times 10^7 \text{ m}^{-1}$ . Balmer suggested that his formula may be more general and could describe spectra from other elements. Then in 1889, Johannes Robert Rydberg found several series of spectra that would fit a more

general relationship, similar to Balmer's empirical formula. This general relationship is known as the Rydberg formula and is given by

$$\frac{1}{\lambda} = R \left[ \frac{1}{n_f^2} - \frac{1}{n_i^2} \right] \quad n_i > n_f,$$
(2)

where  $n_i$  and  $n_f$  are integers, 1, 2, 3, 4, 5, ... up to infinity, with  $n_i > n_f$ . For the hydrogen atom,  $n_i = 2$  corresponds to the Balmer series. There are other series in the hydrogen atom that have been measured. The Lyman series is a set of ultraviolet lines that fit the relationship with  $n_i = 1$ . A series in the infrared region of the spectrum is the Paschen series that corresponds to  $n_i = 3$ . The Brackett and Pfund series are two more in the infrared region corresponding to  $n_i = 4$  and  $n_i = 5$ .

The individual lines in the Balmer series are given the names Alpha, Beta, Gamma, and Delta, and each corresponds to a  $n_i$  value of 3, 4, 5, and 6 respectively. Wavelengths of these lines are given in Table 1.

Name of Line	n <sub>f</sub>	ni	Symbol	Wavelength		
Balmer Alpha	2	3	$H_{\alpha}$	656.28 nm		
Balmer Beta	2	4	$H_{\beta}$	486.13 nm		
Balmer Gamma	2	5	$H_{\gamma}$	434.05nm		
Balmer Delta	2	6	$H_{\delta}$	410.17 nm		

Table 1. Balmer Series – Some Wavelengths in the Visible Spectrum.

In 1913 the Danish physicist Niels Bohr was the first to postulate a theory describing the line spectra observed in light emanating from a hydrogen discharge lamp. With Albert Einstein's theory for the photoelectric effect, where a photon has energy proportional to its frequency, Bohr postulated the existence of energy levels in the atom. He assumed that the energy associated with the photons of light were the result of transitions in the atom from one level to another, with the energy of the photon being equal to the difference in the internal energies specific to energy levels involved in the transition from an initial state to a final state, so that

or

$$\Delta E = -[E_f - E_i] = E_i - E_f.$$
<sup>(4)</sup>

The negative signs in front of the brackets in Equations (3) and (4) are because the photons are being emitted instead of being absorbed. Also, the levels are bound states and are assigned negative values. In other words, the atom is giving up energy instead of having energy supplied to it.

In 1905 Albert Einstein worked out the theory for the photoelectric effect using a concept that Max Planck had used to describe black body radiation. In this theory, for which Einstein received his Nobel prize, he postulated that light consists of packets of energy called photons or quanta and that each quantum of light has energy proportional to its frequency. He determined that the energy of a photon,  $E_{photon}$  is given by

$$E_{photon} = h\upsilon \tag{5}$$

where v is the frequency of the photon and h is a constant of proportionality called Planck's constant. Planck's constant is equal to  $6.6260755(40) \times 10^{-34}$  J·s. From the electromagnetic wave theory of light, frequency v and wavelength  $\lambda$  are related to the speed of light by  $v = \frac{c}{\lambda}$ , so that

$$E_{photon} = h\upsilon = h\frac{c}{\lambda}$$
(6)

and

$$h\frac{c}{\lambda} = E_i - E_f = \Delta E \tag{7}$$

which relates the wavelength of the emitted light to the difference in energy levels between the final and initial states of the atom.

Bohr postulated that an electron can move about the nucleus of an atom in stable orbits, without emitting radiation and losing energy. Thus its energy would be constant in any single orbit and its energy would change only if it changed orbits and a transition occurred by the electron moving from one stable orbit to another. This postulate was revolutionary in that it contradicted electromagnetic theory, which predicted that the accelerating electron would radiate energy. In order to have stable orbits, Bohr further postulated that the magnitude of the orbiting electron's angular momentum would be quantized and that it must be an integral multiple of the quantity  $h/2\pi$ . Since the angular momentum L for an electron of mass m<sub>e</sub> moving in an orbit of radius r with a speed v is

$$L = m_e v r , \qquad (8)$$

his postulate then yields

$$m_e v_n r_n = n \frac{h}{2\pi}$$
 n = 1, 2, 3, ... (9)

where  $v_n$  is the speed of the electron and  $r_n$  is its radius as it orbits with an integral number n of the quantity  $h/2\pi$ . The number n is referred to as the "Principal Quantum Number."

Except for the assumption that the angular momentum is quantized, Bohr's model for the hydrogen atom was developed using simple classical concepts. He assumed that the electron was small in mass compared to the single proton in the nucleus and that it moved about this proton in a circular orbit. He said that the electron was held in an orbit by the electrical force  $F_E$  between the electron and proton, that is given by Coulomb's Law,

$$F_E = \frac{1}{4\pi\varepsilon_0} \frac{e^2}{r_n^2} \tag{10}$$

where e is the magnitude of charges of the electron and proton,  $r_n$  is the radius of the orbit, and  $\epsilon_0$  is a constant known as the permittivity of free space. The electrical force is the force that supplies the centripetal force,  $F_{C_i}$  needed to keep the electron in orbit and is given by

$$F_C = \frac{m_e v_n^2}{r_n} \tag{11}$$

where  $m_e$  is the mass of the electron and  $v_n$  is the speed of the electron as moves in the circular orbit of radius  $r_n$ . Setting Equations (10) and (11) equal gives the relationship

$$\frac{1}{4\pi\varepsilon_0} \frac{e^2}{r_n^2} = \frac{m_e v_n^2}{r_n} \,. \tag{12}$$

By solving Equations (9) and (12) simultaneously for  $r_n$  and  $v_n$  the Bohr model finds expressions for the radii and speeds of the orbiting electron given by

$$r_n = \varepsilon_0 \frac{n^2 h^2}{\pi m_e e^2} \tag{13}$$

and

$$\mathbf{v}_n = \frac{1}{\varepsilon_0} \frac{e^2}{2nh}.$$
 (14)

The minimum radius occurs when n=1 and is referred to as the *Bohr radius*,  $r_1$ , and is given by

$$r_1 = \mathcal{E}_0 \frac{h^2}{\pi m_e e^2} \,. \tag{15}$$

In Bohr's model, the total energy  $E_n$  of the electron as it orbits the proton is the sum of the kinetic energy  $KE_n$  due to its motion and the potential energy  $PE_n$  it has because it is electrically bound to the proton so that

$$E_n = KE_n + PE_n \,. \tag{16}$$

The kinetic energy is given by the classical equation for kinetic energy,  $KE=\frac{1}{2}mv^2$ , and yields

$$KE_{n} = \frac{1}{2}m_{e}v_{n}^{2} = \frac{1}{\varepsilon_{0}^{2}}\frac{m_{e}e^{4}}{8n^{2}h^{2}}$$
(17)

when the orbital speed found in Equation (14) is inserted. The electrical potential energy is given by

$$PE_n = -\frac{1}{4\pi\varepsilon_0} \frac{e^2}{r_n}$$
(18)

which gives

$$PE_{n} = -\frac{1}{\varepsilon_{0}^{2}} \frac{m_{e}e^{4}}{4n^{2}h^{2}}$$
(19)

when the Bohr radius given by Equation (13) is substituted. The negative sign is a result of the electron being bound to the proton, and the potential is taken to be zero when the electron is infinitely removed from the proton. The total energy is then given by

$$E_n = \frac{1}{\varepsilon_o^2} \frac{m_e e^4}{8n^2 h^2} - \frac{1}{\varepsilon_0^2} \frac{m_e e^4}{4n^2 h^2}$$
(20)

which reduces simply to

$$E_n = -\frac{1}{\varepsilon_o^2} \frac{m_e e^4}{8n^2 h^2}.$$
(21)

Since the principal quantum number n characterizes the orbit, a change of energy  $\Delta E$  will occur when it undergoes a transition from an initial value of  $n_i$  to a final value  $n_f$  so that the energy changes from an initial value of  $E_i$  to a final value of  $E_f$ . Using Equation (21),  $\Delta E$  is then given by

$$\Delta E = E_i - E_f = -\frac{1}{\varepsilon_o^2} \frac{m_e e^4}{8n_i^2 h^2} + \frac{1}{\varepsilon_o^2} \frac{m_e e^4}{8n_f^2 h^2}$$
(22)

which reduces to

$$\Delta E = \frac{m_e e^4}{8\varepsilon_o^2 h^2} \left[ \frac{1}{n_f^2} - \frac{1}{n_i^2} \right].$$
 (23)

Substituting Equation (7) gives

$$\frac{1}{\lambda} = \frac{m_e e^4}{8\varepsilon_o^2 h^3 c} \left[ \frac{1}{n_f^2} - \frac{1}{n_i^2} \right]$$
(24)

and is recognized to be in the form of Equation (2),

$$\frac{1}{\lambda} = R \left[ \frac{1}{n_f^2} - \frac{1}{n_i^2} \right],\tag{25}$$

with the Rydberg constant R given by

$$R = \frac{m_e e^4}{8\varepsilon_o^2 h^3 c}.$$
 (26)

In this experiment, Equation (25) will be used to determine R from measurements of  $\lambda$ . For the visible, Balmer series  $n_i$  is 2 and values of  $n_f$  will be matched to the observed spectral pattern.



Figure 1. Apparatus and setup for the Balmer series experiment.

#### Apparatus

The apparatus is shown in Figure 1 and consists of: (1) a Pasco Model SP-9268 precision student spectrometer, (2) a grating with either 300 lines/mm or 600 lines/mm, (3) a hydrogen discharge lamp and power supply, (4) a magnifying glass, (5) a small night light, and (6) a black cloth to block out stray light. The spectrometer is a precision instrument and is shown in Figure 2 with the important parts labeled.



Figure 2. Pasco precision student spectrometer.



Figure 3. Schematic diagram of student spectrometer.

A schematic diagram of the student spectrometer is shown in Figure 3, which illustrates the principles of its operation. The student spectrometer consists of three basic components: a collimator, a diffraction grating, and a telescope. The light to be analyzed enters the spectrometer through an adjustable slit, which forms a narrow, well-defined line source of light. This slit is located at the focal point of the collimator, which transforms the light into a parallel, collimated beam of light. The beam uniformly illuminates the grating so that all light rays strike the grating at the same angle of incidence. A parallel beam of light is necessary to illuminate the grating so that a sharp image of the slit can be formed when viewed with the telescope.

The diffraction grating disperses the light so that the diffraction angle,  $\theta$ , depends on the wavelength of light,  $\lambda$ , and the grating spacing, d, according to the grating equation,

$$d\sin\theta = m\lambda \tag{27}$$

where n is an integer given by

$$m = 0, 1, 2, 3, \cdots$$
 (28)

The integer, m, is referred to as the diffraction order. Light of a given color will be diffracted at a specific angle for a given order. All light rays of that color will be parallel if the incident light rays are parallel. Light of a different color is diffracted at a different angle, but its light rays will also be parallel.

When the telescope is focused at infinity, parallel light of a specific color entering the telescope will form an image of the slit of that color in the focal plane of the objective lens of the telescope. Thus a green image of the slit will be formed at one angle and a red image of the slit will be formed at another, larger angle. The telescope is attached to a rotating arm whose angle of rotation can be precisely and accurately measured. This device, often referred to as a goniometer, measures the diffraction angles of the spectra of colors of light. By rotating the telescope arm, images of the slit of various colors can be viewed and magnified with the eyepiece and their respective angles of diffraction measured. The eyepiece has a graticle with an orthogonal set of cross-hairs, which help align and reference the viewed images of the slit. From the grating spacing and measurements of the diffraction angles, the wavelength of the observed light can be determined from the grating equation, Equation (27).

## Procedure

- 1. The student spectrometer will provide the best and most accurate results if it is properly aligned and focused. The light source should be located about 1 cm from the collimator slit. A block of wood is provided so that the discharge light source can rest partially on the spectrometer platform. The slit should be examined and adjusted so that it is just barely open. Note that only one side of the slit moves while the other side remains fixed as adjustments are made.
- 2. Look through the eyepiece of the telescope and view the cross-hairs of the graticule. (This should be done preferably without your glasses if you wear them. The eyepiece is adjustable so that you can correct for your eyesight.) Slide the eyepiece in and out until the cross-hairs come into sharp focus. By rotating the graticule alignment ring,

adjust the orientation of the cross-hairs so that they are aligned vertically and horizontally. You may need to refocus the cross-hairs.

- 3. The telescope should be focused for an object located at infinity. Loosen the telescope rotation lock-screw (see Figure 2) and rotate the telescope arm to view a distant object on a wall across the room, or a building outside. Adjust the telescope focus knob so that the viewed image of the distant object is clearly in focus.
- 4. Rotate the telescope arm so that it is directly across and aligned with the collimator. <u>The telescope focus should remain unchanged, kept focused at infinity, during this</u> <u>step and at all times following</u>.
- 5. Turn the light source on and view the slit of the collimator. The grating should not be in its mount. The telescope arm may need to be rotated slightly to see the red light and outline of the slit. The light source may need to be moved slightly to give the best, most intense illumination of the slit. You may loosen and re-tighten the telescope rotation lock-screw as needed to facilitate fixing and moving the arm position.

# CAUTION: The hydrogen discharge lamp is powered by high voltage and the tube gets hot. DO NOT touch the tube anywhere especially near the ends where the electrical contacts are made.

Note: Simple hydrogen discharge tubes can lose their hydrogen by reacting with impurities inside the tube and by small leaks from the outside. A good tube will have a bright red color near its center, and a poor tube will be more pinkish near the center. For best results, it is important to have a good tube.

- 6. Use the focus knob to adjust the collimator focus for the clearest, sharpest image of the slit. If needed, re-adjust the light source to provide the best illumination of the slit and to give the sharpest images.
- 7. Gratings with either 300 lines/mm or 600 lines/mm are provided for this experiment, and the grating spacings d are either 1/300000 m or 1/600000 m. The number of lines per mm should be labeled on the grating, but if not, ask your instructor for this value. The grating is a replica grating approximately 1 inch square that is mounted in the center, on one side of a 1½"x2"x5/32" glass plate. The grating itself should not be touched and the glass mount should be handled only by its edges. The diffraction grating should now be placed in the grating mount with the grating side of the glass mount against the vertical posts. Loosen the spectrometer table lock-screw and align the plane of the grating so that it is perpendicular to the optical axis formed by the collimator and telescope when they are directly opposite one another. There is a line inscribed on the spectrometer table to assist with the orientation. This adjustment doesn't have to be precise, but in your best judgment, it should appear to be perpendicular.

8. The image you see with the telescope directly in line with the collimator is the undiffracted, central image. Now with the black cloth over the apparatus to shield out stray light, rotate the telescope arm to the left and right to survey the different lines and colors of diffracted light. Moving away from the central image, you should see the first order diffraction lines of violet, turquoise, and red light followed by the second order diffraction pattern of lines of the same colors. These visible lines are three of the Balmer lines corresponding to  $n_f = 5$ , 4, and 3. There is a fourth one corresponding to  $n_f = 6$ , but it is weak, and sometimes so extremely weak that it cannot be seen. The room may have to be completely dark to see this line, if at all possible.

Note: There are bands of very weak transitions due to molecular hydrogen that can sometimes be observed between the blue, green, and red lines. The emissions from these bands grow stronger as a tube ages, and at the same time, the hydrogen lines grow weaker.

- 9. The following steps involve aligning and setting the reference value for making the precise angular measurements of the diffracted light. It is important to do these steps carefully, since all measurements will be made relative to this setting.
- 10. Rotate the telescope arm back to the position where it is directly opposite and in line with the optical axis of the collimator and where the central, undiffracted image can be observed. Adjust the arm so that the vertical cross-hair is near or on the central image and tighten the telescope rotation lock-screw. Use the fine adjust knob near and just to the right of the lock-screw to align the vertical cross-hair exactly with the left, stationary slit, the left edge of the central line image. See Figure 2.

Note the exact position of the vertical cross-hair and left edge as this will be the relative position of these for all subsequent alignments.

11. Angles are measured with the 0-360° scale engraved into the rotating telescope base and are read relative to the zero fiducial ruling on the vernier scale that is fixed to the rotating table base. Set the zero reference angle by loosening the table rotation lockscrew and rotating the table base until the zero fiducial mark on the vernier scale is closely aligned with the zero mark on the 0-360° main scale. Tighten the lock-screw and use the table rotation fine adjust knob to position the two zero marks so that they are exactly aligned with each other. Use the magnifying glass to better make this adjustment. As a check, the 30' ruling on the vernier scale also should be aligned exactly with the 14.5° ruling on the main scale. See Figure 4.



Figure 4. Telescope view of alignment of slit with cross hairs and alignment of vernier scale with rotating scale.

- 12. At this point the following conditions should exist: (1) the telescope should be aligned with the optical axis of the collimator, (2) the vertical cross-hair in the eyepiece should be aligned with the left edge of the central image,(3) the zero marks of the vernier and main scales should be aligned exactly, (4) the plane of the grating should be perpendicular to the optical axis, and (5) all adjustments should be fixed with their respective lock-screws. The spectrometer should be ready for measurements.
- 13. The general procedure for measuring the angles of the various diffraction lines is to un-tighten the telescope arm rotation lock-screw, rotate the telescope to view the diffraction line of interest, center the image of the line near the vertical cross-hair, tighten the lock-screw, use the telescope rotation fine adjust knob to align the vertical cross-hair with the left edge of the slit image, and then read the angular scale.
- 14. The angles for each of the diffracted lines can be read most simply by avoiding the vernier scale feature and estimating the angles to the nearest 0.1° on the scale on the rotating table base. The precision and accuracy provided by this estimate will be more than adequate for obtaining excellent results in this experiment. The angle can be read more accurately by using the magnifier. The night light will be needed in the darkened room.
- 15. The zero on the vernier scale is the reference mark used to indicate the exact angular position on the main scale. Remember that the smallest division on the main scale is 0.5° and that the estimate only has to involve 5 equal imaginary increments of 0.1° in each of those.
- 16. Open up an Excel spreadsheet and label the columns and rows as shown in Figure 5.

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3	Color	Color	n <sub>i</sub>	m	Reading	Reading	Corrected	θ <sub>R</sub> (rad)	$\theta_{\rm L}({\rm rad})$	λ	1/λ	$(1/4 - 1/n_i^2)$	
4	v		6	1									
5	bv		5	1									
6	bg		4	1									
7	r		3	1									
8	v		6	2									
9	bv		5	2									
10	bg		4	2									
11	r		3	2									
12													

Figure 5. Example of Excel spreadsheet for hydrogen Balmer series experiment.

17. In your spreadsheet, measure and record the readings on the main scale for the angles  $\theta_R$  and  $\theta_L$  in degrees. This should be done for  $n_i = 5$ , 4, and 3, both right and left diffracted Balmer lines, and for both the first and second order patterns, m = 1 and m = 2. If possible the measurement should also include the  $n_i = 6$  line. The readings for  $\theta_R$  should be in the range of 0-30° and the readings for  $\theta_L$  should be in the range 330-360°. Of course the values of  $\theta_L$  should be in the range of 0-30°, but will be found later in the analysis of the data by subtracting the reading value from the initial value of 360°.

## Analysis

- 1. In the extra column for the corrected value for the angle  $\theta_L$ , subtract the reading for  $\theta_L$  from 360°. These values will be in the range from 0 to 60°, and should be nearly the same values as  $\theta_R$ . Examine your values of  $\theta_L$  and  $\theta_R$  to see if they are approximately the same on both sides. This will allow you to check for any mistakes in the angle measurements. The pairs of values should be within about 0.5° of each other, You should repeat the measurement if there appears to be a mistake.
- 2. In the columns for  $\theta_L(rad)$  and  $\theta_R(rad)$  convert the angles in degrees to radian units. Excel requires the angles for trigonometry functions to be in radians. The conversion factor is  $180^\circ = \pi$  radians, therefore multiply the angle in degrees times the value for  $\pi$  and then divide by 180. In **Excel**, the value of  $\pi$  can be obtained with the *Math & Trig* function, PI() with no argument.
- 3. Use Equation (27) to calculate  $\lambda$  from each of the values for  $\theta_L(rad)$  and  $\theta_R(rad)$  and record the values in the column labeled for these values. The value for the sine of the angle in cell H4 is written as =SIN(H4). Remember that the argument must be in radians and placed inside parentheses.

- 4. In the columns for  $1/\lambda$  and  $(1/4 1/n_i^2)$ , compute these values.
- 5. Equation (1) suggests that a plot of  $1/\lambda$  versus  $(1/4 1/n_i^2)$  should give a straight line passing through zero with a slope of *R*. Make a graph of  $1/\lambda$  versus  $(1/4 1/n_i^2)$  and label the axes with proper titles and units.
- 6. Use the **Add Trendline** feature of Excel to find the slope of the straight line that best fits your data. Force the intercept to be zero.
- 7. Compare your value for the slope and R with the accepted value of the Rydberg constant. Calculate the percent difference and enter your result in your spreadsheet.

% Difference = 
$$\frac{|\text{Accepted Value - Measured Value}|}{\text{Accepted Value}} \times 100\%$$
 (29)

- 8. Use your measured value for the Rydberg constant to calculate the wavelengths of the observed emission lines. Compare these values with your measurements of the wavelength and calculate the percent difference using Equation (29).
- 9. Print your graph and spreadsheet of data.

## Questions

- 1. Show that the SI units for Planck's constant h are equal to the SI units of angular momentum.
- 2. Calculate the magnitude of the Bohr radius.
- 3. Calculate the speed of the electron moving in an orbit whose radius is equivalent to the Bohr radius.
- 4. Using your value for the Rydberg constant, calculate the wavelength of an ultraviolet transition in the Lyman series from the n = 2 level and to the n = 1 level.
- 5. Using your value for the Rydberg constant, calculate the wavelength of an infrared transition in the Paschen series from the n = 4 level and to the n = 3 level.
- 6. How much energy does it take to ionize a hydrogen atom in its ground state? That is how much energy has to be supplied to move an electron from the n = 1 level to the  $n = \infty$  level?

7. In the analysis of your results, suppose you had plotted  $1/\lambda$  versus  $1/n_i^2$  instead of  $(\frac{1}{4} - 1/n_i^2)$ . Would your data give a straight line and would its slope give the same results for R? How would the intercept change?

## **Prelab Questions**

- What is the energy of a red photon of wavelength 600 nm? Of a blue photon of wavelength 400 nm? Express your answers in both Joules and electron-volts. (1 eV=1.60 x 10<sup>-19</sup> J)
- 2. How is the wavelength of the light to be measured in this experiment? Describe each of the terms in Equation (27).
- 3. Of the following three transitions: from n = 2 to n = 1, from n = 3 to n = 2, from n = 4 to n = 3, which produces photons with the shortest wavelength? The longest? Which is in the visible part of the spectrum? Which is in the ultraviolet? Which is in the infrared?