Objective
To calculate the Rydberg constant from the spectrum of atomic hydrogen.

Preparation
1. Read all of this write-up.
2. Understand the experiment, apparatus, and procedures well. **You will be performing many of the operations in the dark.**

Overview
Excited hydrogen atoms are produced in an electric discharge which not only dissociates hydrogen molecules, but excites the atoms as well. These atoms radiate light at discrete wavelengths, some of which lie in the visible region of the spectrum. This visible light is dispersed by a diffraction grating in a spectrograph and detected by photographic film. The wavelength determines the position of the lines in the spectrum, and the wavelength is calibrated using the Hg spectrum where the lines are intense and well-known. Measurement of the H atom lines then makes it possible to determine the Rydberg constant.

Theory
Hydrogen exists mainly as diatomic molecules, but if hydrogen gas is heated very hot or bombarded by electrons, the molecules can be dissociated into atoms. Thermal heating will result mainly in ground state atoms, but electron bombardment of the atoms (as happens in an electric discharge) can produce atoms in excited states. Excited atoms can undergo transitions to states of lower energy by spontaneously radiating energy characteristic of the energy difference between the two states, given by the well-known Einstein relation,

\[ E_2 - E_1 = \Delta E = h\nu \]  \hspace{1cm} (1)

where \( h \) is Planck's constant and \( \nu \) the frequency of light emitted.

For an atom with one electron, the Schrödinger equation can be solved exactly and the energy is given by\(^1\)

\(^1\) Some exceedingly small effects are ignored here (spin-orbit coupling and electrodynamical effects) which result in the energy being slightly dependent upon a second quantum number \( l \), where \( l \) is also integral but \( l \leq n \). This results in the Lamb
Chapter 5. Hydrogen Atom Spectrum

\[ E_n = -\frac{\mu e^4}{8\hbar^2\varepsilon_0^2} \frac{1}{n^2} \quad n = 1, 2, 3, \ldots \quad (2) \]

where \( e \) is the charge on the electron and \( \varepsilon_0 \) the permittivity of vacuum. The reduced mass, \( \mu \), of the electron and proton is given in terms of the electron mass, \( m \), and the proton mass, \( M \), by

\[ \mu = \frac{mM}{m+M} \quad (3) \]

The negative sign means that a state of principal quantum number, \( n \), is more stable (lower energy) than one with \( n = \infty \), where the electron and proton are infinitely far apart and the energy is defined to be zero. For finite values of \( n \) the system is thus bound. In accordance with Eq (2) the ground state is bound by 13.595 eV (the ionization potential) whereas the first excited state is bound by only 3.4 eV.

Fig 1. A few electronic energy levels of the hydrogen atom. As \( n \) increases the energy levels converge to a limit, and above this limit (the shaded area) there are a continuum of levels corresponding to complete separation of proton and electron with kinetic energy \( > 0 \)

shift, but this is much too small to be detected in these experiments. For atoms with more than one electron, the energy is significantly dependent upon \( l \) (!).
Atoms may undergo transitions between any two states of different principal quantum number, depending on whether they absorb or emit radiation. There are no "selection rules" for \( n \). An energy level diagram for the H atom is shown schematically in Fig 1, together with a number of representative transitions in which a photon could be emitted. (We will detect these photons in this experiment.) These transitions were historically identified in different spectral regions, with the Lyman series appearing in the ultraviolet, the Balmer series in the visible, the Paschen in the infrared, and so on. Each series is characterized by the lowest level, \( n=1 \) for the Lyman series, \( n=2 \) for the Balmer series, etc.

Our apparatus will restrict us to observing transitions in the visible region of the spectrum, the Balmer series. (Roughly speaking, lines from the Lyman series would be absorbed by the atmosphere and are for us unobservable; lines in the Paschen series lie in the infrared are not recorded by our photographic film.) Combining Eqs (1) and (2) for the Balmer series (\( n_{\text{final}} = 2 \)) we find

\[
\Delta E = E_2 - E_n = \frac{\mu e^4}{8h^2\varepsilon_0^2} \left( \frac{1}{4} - \frac{1}{n^2} \right) = \frac{hc}{\lambda} \tag{4}
\]

and

\[
\frac{1}{\lambda} = \frac{\mu e^4}{8h^3c\varepsilon_0^2} \left( \frac{1}{4} - \frac{1}{n^2} \right) = R \left( \frac{1}{4} - \frac{1}{n^2} \right) \tag{5}
\]

where \( R \) is the Rydberg constant and has the calculated\(^2\) value of 109 677.5805 cm\(^{-1}\) for H. One usually measures the wavelength and connection with theory is made with the reciprocal wavelength (called the wavenumber, \( \tilde{\nu} \), and measured in cm\(^{-1}\).)

**METHOD**

Measurement of the wavelengths of the lines in the Balmer series is experimentally carried out by comparing the hydrogen spectrum with a reference spectrum for which the wavelengths are already known. The iron or mercury spectra are frequently used because they have many intense lines which have been measured on an absolute scale by interferometry. The iron spectrum is very rich (too rich) and we will use the mercury spectrum which can be more readily identified.

\(^2\)The experimental value for the Rydberg (from Eq 5), \( R_\infty = 109 737.31534 \text{ cm}^{-1} \) (for an electron and nucleus of infinite mass) is more accurately known than the theoretical value because of uncertainties in \( e, \ h, \ and \ \mu \).
The spectrograph is shown schematically in Fig 2. A light source is focused on a slit, and the light passing through the slit strikes a diffraction grating and is reflected back onto a strip of 35 mm film. The film is held on an arc of a circle centered on the grating so that wavelength is roughly a linear function of distance along the film, although experimental uncertainties such as ruling inaccuracies of the grating, shrinkage of the film during development, and so on, still require that the spectrograph be calibrated with the Hg lamp.

The strip of film can be exposed in several different swaths and the developed film will appear as in Fig 3.

As described below, the spectrograph has a device (sketched in fig 5) which allows you to move the dispersed image to expose different regions of the film, hence the 4 exposed strips in the sketch in Fig 3. For highest precision, you will interleave the hydrogen spectrum with the Hg calibration spectrum (5 above). The other strips are exposed with the individual lamps (3 for hydrogen, 7 for mercury, and 9 for sodium) and these spectra allow you to identify which lines come from which spectra. However, as described in the procedure below, you will not be taking the spectra in the order listed above.

The elemental lamps are discharge tubes filled with $\approx 0.5$ torr and connected to high voltage, low current transformers. The high voltage applied across the metal electrodes in the tube cause spontaneous ionization of the gas by field emission, and once electrons are produced they are accelerated into gas molecules, collisionally ionizing them and giving still more electrons, and the process becomes an avalanche, with the
final current limited by the capacity of the transformer. The hydrogen lamp will glow with a bright red color, but the mercury lamp produces ultraviolet radiation which is dangerous to the eyes. DO NOT LOOK directly into the mercury lamp. All of the lamps get hot and all run at dangerous voltages. Keep your fingers out of the electrodes!

**PROCEDURE**

1. Loading the film into the holder

The film holder holds the film as it is exposed. An end-on view of the holder is shown above. The upper groove holds the removable outer cover, or dark slide. The lower groove holds the film. A lever on one end of the holder restricts access to the lower groove when it is in the closed position (i.e. flush with the holder).

To load film into the holder, remove the outer cover and move the lever to the open position. Then in the dark, insert the film into the lower groove, emulsion side out. The emulsion, a light sensitive coating, feels "dull" and faces inside the natural curve of the film. The film will be correctly inserted if it naturally curves the same direction as the film holder. Move the lever to the closed position, and cut off any excess film. Replace the outer cover, being careful not to bend it. If you meet resistance, it is in the wrong groove; remove it immediately and try again. Turn on the light only when the outer cover is replaced.

"Darkroom"

The bulk film loader, the spectrograph film holder, and the developing tank must all be loaded and unloaded in complete darkness. Practice using each of these items using exposed film which the instructor will provide. Improperly loading the film will probably add about three hours to the time required for this experiment.

The “darkroom” is a light proof film changing bag which has a zippered opening for loading apparatus and light-tight sleeves into which you put your hands.

**Bulk Film Loader**

The bulk film loader is a light-tight film dispenser. Do not open it in the light, or you will expose the entire roll of film (you can practice loading film in the light using a practice loader, provided by the instructor). In the dark, turn the upper black plate clockwise as far as it will go, closing the gate. Open the door of the
holder, and then turn the plate counterclockwise to open the gate. Reach in and remove enough film to fill the spectrograph film holder (measure against the holder's removable outer cover). Cut off this much film, and return the remainder to the upper end of the loader. Turn the upper plate clockwise to the closed gate position, and close the door of the holder. Close both the gate and door, load the film holder, install the outer dark slide, and only then turn on the lights.

Exposing the Film

Expose the film with the various lamps according to the following procedure:

a. Replace the spectrograph's Plexiglas cover with the film holder.

b. Close the shutter, and then slide the cover of the film holder (the "dark slide") out to the mark. If you slide it all the way out, it will be impossible to replace. Make certain you have not pulled out the film; if you have, discard the film and start over.

c. Cover the film holder with the black felt to minimize light leaks.

d. Make the exposures as described under the section Lamps. Do not close the outer cover between exposures to avoid moving the film.

e. After all exposures have been made, slide the outer cover closed.

f. Replace the film holder with the Plexiglas cover, to keep dust from the diffraction grating.

g. Develop the film

Lamps

SAFETY: Both arc lamps operate at extremely high voltages. The mercury lamp emits ultraviolet radiation, which can harm your eyes; do not look directly at the mercury lamp while it is in use. The sodium lamp needs to warm up for five minutes before use, and gets extremely hot. The sodium lamp will not focus as narrowly as the two arc lamps.

PROCEDURE For each exposure, follow the procedure outlined below:

1. Place your light source as shown in Figure 2, at the same height as the slit assembly. Focus the strip of light onto the paper covering the shutter by sliding the cylindrical lens along the optical track. Adjust the position of the strip horizontally by shifting the light source, and vertically by moving the lens up or down. The strip of light should pass through all three circles drawn on the shutter. Remember that any movement of the light source or lens may change the focus. Once the light is correctly positioned and focused, tighten the screw holding the lens assembly to the optical track.
2. Move the slit width adjustment to the desired width; for this experiment, make all exposures with a 32 micron width.

3. Select the image location on the film by moving the Hartmann slide to the desired setting (see Figure 5). Higher numbers place the spectrum lower on the film.

4. Open the shutter.

5. Wait for the specified exposure time described below.

6. Close the shutter.

EXPOSURES:

1. Make exposures with the mercury arc lamp using image placement settings of 5 and 6, and an exposure time of 25 seconds each. (The hydrogen and mercury arc lamps use the same power supply, and the exposure time for the hydrogen lamp is rather long. You will be taking the spectrum of the mercury lamp first, since it will not be turned on long enough to heat up appreciably, and it can therefore be easily replaced by the hydrogen lamp.)

2. Replace the mercury arc lamp with the hydrogen arc lamp; refocus and position. Do not touch the film holder.

3. Make exposures with the hydrogen arc lamp using image placement settings of 5 and 4, and exposure times of 25 and 5 minutes respectively (the longer exposure shows the weaker lines better).

3a. While waiting for these exposures, prepare the developing chemicals. Place a thermometer in the developer.

4. Replace the arc lamp with the sodium lamp; refocus and position.
5. Make exposures with the sodium lamp using image placement settings of 5 and 7, and an exposure time of 15 seconds each. Close the dark slide on the film holder.

**Developing the film**

**Developing Tank and Reel**

In the dark, locate the entrances on both the top and bottom discs. Rotate one disc until these entrances are as far apart as possible. Feed the film, with the emulsion side toward the center of the reel, into the upper entrance, and pull it into the lower entrance without rotating the discs. When the film is firmly loaded into both entrances, begin rotating the discs back and forth with respect to each other. The film should automatically feed into the reel. Continue rotating the discs until the film is completely wound.

Place the loaded reel into the developing tank. Lock the cover on the tank by rotating it clockwise as far as it will go. At this point, it is safe to turn the lights back on.

**Developing Chemicals**

The exposed image on the film must be treated with a *developer* to develop the image, with a *stop bath* to stop the action of the developer, and then with a *fixer* to make the image permanent and eliminate any further sensitivity to light. These chemicals are washed from the film with water, and the film treated with a wetting agent (Photo Flo) to reduce wetting of the film by water so that it dries quickly and uniformly.

![Fig. 6 Developing time versus developer temperature.](image)

To sufficiently cover the film reel when it is in the developing tank, you will need approximately 300 mL of each developing chemical. In the appropriate labeled beakers, mix 300 ml of developer, stop bath, fixer, and Photo-Flo. For the developer, simply dilute the stock developer solution 1:1 with de-ionized water.
Mix the stop bath and fixer according to the directions on the stock container. Use the premixed Photo-Flo undiluted.

To develop the film, check the temperature of the developer, and then add it to the developing tank. Tap the tank sharply to remove air bubbles that adhere to the film. Agitate the developer by shaking the tank for five seconds every 30 seconds for the time found in the graph above for the developer's temperature. At the end of this developing time, pour the developer back into the correct beaker. Add the stop bath to the developing tank and agitate for 30 seconds. Return the stop bath to its beaker, and add the fixer to the tank. Agitate for five seconds every 30 seconds for five minutes. Return the fixer to its beaker and add the Photo-Flo. Agitate for 30 seconds. Return the Photo-Flo to its beaker. Open the tank, and wash the film for 10 minutes with water. Drain the film well, and hang to dry for about 30 minutes. Do not dry the film with paper towels; they will scratch the emulsion. Dispose of the developing chemicals as directed by your teaching assistant.

**Comparator**

The comparator is a clear, finely graduated ruler with an attached movable microscope. The accuracy of your measurements with the comparator will determine your grade; poor use of this piece of apparatus will result in a terrible value for the Rydberg constant. Any motion of the comparator with respect to the film destroys all previous measurements. Be extremely careful when moving the objective. Begin at one end of the film, and move the objective once across the film. Measure all line positions and widths to the nearest 0.002 mm.

It is difficult to measure dark lines against dark graduations. The easiest way to do this is to align the spectrum of interest so that the lines extend half-way into the graduations.

**Assigning Line Positions**

Assign the mercury reference lines using the figure below as a guide. Your film is from a grating spectrograph, and you may have extra, second-order lines, which can be ignored. Use the sodium D line positions as an aid in assigning the mercury lines. These lines are located at 588.995 and 589.592 nm.

<table>
<thead>
<tr>
<th>579.06</th>
<th>576.96</th>
<th>546.07</th>
<th>491.6</th>
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</tbody>
</table>

Fig 7. Schematic mercury spectrum with wavelengths measured in air. Relative intensities are not indicated

To assign the mercury lines, find two lines that can be assigned easily and solve for the slope and intercept of the line fitting these lines. Use this fit to predict the positions of
the remaining mercury lines, and then perform a least-squares linear fit using \texttt{Experlsq.m} on all assigned mercury lines to find the best calibration line. You may use the sodium lines in preliminary fits, but do not include them in the final least-squares fit because they are too broad.

Using your calibration fit, determine the positions of the lines in the Balmer series. To assign the lines, guess the \( n_1 \) values for the first few lines, and then solve for a Rydberg constant and an intercept. (This is a crude plot serving only to guide you in assigning values of \( n \) for your remaining lines and it’s not necessary to weight the points at this stage.) Use these values to assign the remaining \( n_1 \) values, weight the points and then perform a least-squares fit of frequency vs. \( 1/n_1^2 \) as outlined in SGN6 (Chapter XXII) to obtain your final value for the Rydberg constant. You should strive to assign as many lines as possible for good accuracy, and you will need to properly weight the points.

The errors in this experiment are correlated in that imperfect comparator measurements are used to calibrate the wavelength scale. Let us assume that a comparator reading of a single line has a standard deviation \( \sigma_0 \). You calibrate the comparator by passing a least-square line through a plot of mercury line wavelength vs. \( d \), where \( d \) is the comparator reading as shown in Fig 8L.

The wavelength of a given hydrogen line is then obtained from this calibration plot and the comparator reading for the hydrogen line, \( d_H \). There is again a standard deviation for the hydrogen line comparator, but even if the comparator measurements for hydrogen had no error, there would still be an uncertainty in the hydrogen wavelengths due to the uncertainties in the mercury measurements. As an example, Fig 8L shows schematically that the uncertainties in locations of Hg calibration lines could yield an uncertainty in the straight calibration line drawn through the data. The wavelengths for the hydrogen lines are obtained from the calibration line (with its uncertainty) and the positions of the hydrogen lines (with their uncertainties) as shown in Fig 8R.
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Error Analysis

Fig 8. (L) Schematic wavelength calibration plot showing best line together with extreme lines for mercury calibration points. (R) One hypothetical hydrogen line is shown, together with its uncertainty showing how the uncertainty in wavelength is related to both the uncertainty in the line position as well as the uncertainty in the "best" line. (These plots are grossly exaggerated because an actual plot would have such small error bars as to be unnoticeable. Also, points near the center still have an uncertainty in \( \lambda \), although the uncertainty is less than at the extremes of the range.)

The Matlab linear least squares fitting routines provides you with standard deviations for both the slope and the intercept of the fit to the mercury lines. These deviations suggest that you could pass slightly different lines through the data as suggested in Fig 8 L. When determining a H wavelength from its distance measurement, the slightly different calibration lines in Fig 8L will produce a range of H atom wavelengths as suggested by Fig 8R. We will take this range as \( 2\sigma \) for each of the H atom lines. Each H atom line then has a different uncertainty depending on its position on the film and your Hg calibration, as suggested in Fig 8 (R). (These value of \( \sigma \) could be obtained graphically if you have a very large plot, but because the calibration boundaries will almost coincide on your plot you need a little graphical calculation to get \( \sigma \).) Weight each H atom line by the reciprocal of its standard deviation when plotting \( 1/\lambda \) vs \( 1/n^2 \). The standard deviations given by the final fit are not necessarily related to the accuracy of the measurements, but only to the correlation of the data points. Perfectly accurate measurements will not necessarily produce a perfect fit while inaccurate measurements may produce a great fit.

Report

Include in your report all data, your method for analyzing the spectra, sample calculations, film, and all relevant graphs. For both hydrogen and mercury lines, prepare tables of measured line positions, wavelengths (both known and calculated for mercury), and wavenumbers for hydrogen. Give limits of error for calculated hydrogen wavelengths and the error limits for the Rydberg constant. Include the literature value of the Rydberg constant along with its source. There is a difference between \( R_H \) and \( R_\infty \).
Discussion

1. Why does the intensity of the lines in the Balmer series decrease as the wavelength decreases? (The first line near 6500 Å is actually the strongest, but the film is less sensitive for red wavelengths, so the first line may not appear the strongest.)

2. What are some experimental factors that influence the line width?

3. Show that typical lines in the Lyman, Balmer and Paschen series lie in the uv, visible or infrared, respectively.

Preliminary Exercise

The following data have been taken:

**MERCURY SPECTRUM**

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<th>Wavelength</th>
</tr>
</thead>
<tbody>
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<td>579.06</td>
</tr>
<tr>
<td>113.5</td>
<td>576.96</td>
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<tr>
<td>134.4</td>
<td>546.07</td>
</tr>
<tr>
<td>208.4</td>
<td>435.84</td>
</tr>
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<td>227.9</td>
<td>407.78</td>
</tr>
<tr>
<td>230.1</td>
<td>404.66</td>
</tr>
<tr>
<td>255.9</td>
<td>366.31</td>
</tr>
</tbody>
</table>

**HYDROGEN SPECTRUM**

<table>
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<th>Comparator reading</th>
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</thead>
<tbody>
<tr>
<td>59.7</td>
</tr>
<tr>
<td>174.9</td>
</tr>
<tr>
<td>210.1</td>
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<tr>
<td>226.3</td>
</tr>
<tr>
<td>235.2</td>
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<tr>
<td>240.7</td>
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</tbody>
</table>

Assign wavelengths and values of the principle quantum number, n, to the lines in the Hydrogen spectrum and then calculate the Rydberg.

Note that the Comparator readings don’t have much precision; you need to do better in the lab!

Turn in your plot of frequency vs $(1/n^2)$ and a table of comparator readings, wavelength, and quantum number for the lines in the hydrogen spectrum.