

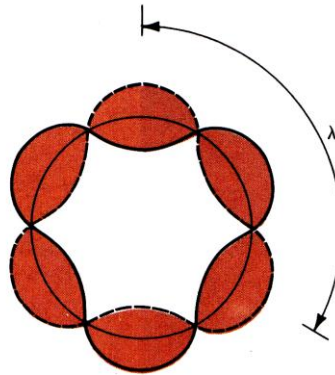
## Atomic Spectra

### I. Introduction and purpose

By far the most important atomic system to understand is hydrogen, since it is the simplest atom that exists. Many of the most revolutionary breakthroughs in modern physics have resulted from careful study of this one atom. In this lab we will examine the spectrum produced by electronic transitions in hydrogen, and of a multielectron atom, sodium, which we expect should be similar in many ways.

### II. Hydrogen

The simplest theory that seems to model the basic behavior of the hydrogen atom is that of de Broglie, which was later enhanced by Bohr. If we imagine that electrons are described by “circular standing waves” around the nucleus, then only certain orbits will be allowed.



**Figure 1. De Broglie's model of the hydrogen atom.**

As can be seen from Figure 1, for standing waves to exist, the circumference must equal an integer number of wavelengths. Thus,

$$2\pi r = n\lambda$$

where  $n$  is an integer larger than zero. Of course, de Broglie then went on to hypothesize that particles behaved as waves with the relationships

$$E = hf \quad \text{and} \quad p = h/\lambda,$$

so that

$$L = pr = mvr = \frac{h}{\lambda} \frac{n\lambda}{2\pi} = n\hbar \quad (1)$$

where  $\hbar = h/2\pi$ . Now, we know that for an electron to “orbit”, there must be a force that supplies the needed centripetal acceleration to keep it travelling in a circle. Clearly, this must be the coulomb attraction between the positively charged proton in the nucleus and the negatively charged electron:

$$F = \frac{mv^2}{r} = \frac{ke^2}{r^2} \quad (2)$$

which is directed radially in toward the proton. The total energy of the electron is given by

$$E = KE + PE = \frac{1}{2}mv^2 - \frac{ke^2}{r}. \quad (3)$$

If we combine Equations 1, 2, and 3 we get the following expression for the total energy

$$E = -\frac{1}{2} \frac{mk^2e^4}{\hbar^2} \frac{1}{n^2}. \quad (4)$$

The energy difference between two energy levels, which will be either emitted or absorbed in the form of electromagnetic radiation when the electron makes a transition, is therefore

$$E_\gamma = \frac{mk^2e^4}{2\hbar^2} \left( \frac{1}{n_2^2} - \frac{1}{n_1^2} \right) \quad (5)$$

where  $n_1$  and  $n_2$  are the quantum numbers for the initial and final state.

This particular treatment of the hydrogen atom has several problems, and has largely been superseded by the quantum mechanical treatment that we discussed in class. In this model, we must solve the three dimensional Schrödinger equation for the Coulomb potential. When we do this, however, we get the same result as Equation 5 in the case of hydrogen if we neglect relativity. We also find that we have two other quantum numbers,  $\ell$  and  $m$ , which are related to the angular momentum. These results are displayed in Table 1.

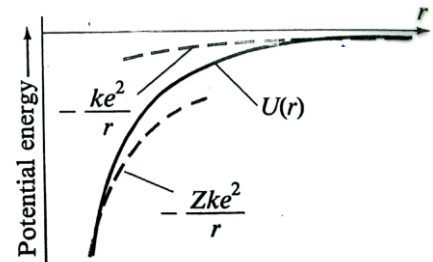
**Table 1. The quantum numbers that describe the state of the hydrogen atom.**

<i>Quantity</i>	<i>Quantum Number</i>	<i>A. Measurable Quantity</i>
II. Energy	$n = 1, 2, \dots, \infty$	$E_n = \frac{-13.6 \text{ eV}}{n^2} = \frac{-E_R}{n^2}$
Angular Momentum	$\ell = 0, 1, \dots, n - 1$	$L = \sqrt{\ell(\ell + 1)}\hbar$
Z-Component of Angular Momentum	$m = -\ell, -\ell + 1, \dots, \ell$	$L_z = m\hbar$

### III. Sodium and other multielectron atoms

Multielectron atoms cannot be easily solved like the hydrogen atom, but must be approximated. The standard way this is accomplished is by using hydrogen-like single electron wave functions to determine an average potential, then this potential is used to correct the original wave functions. By doing this process several times, good agreement can be obtained with measurement.

It is discovered that when the electron is near the nucleus of charge  $+Ze$ , it behaves as if it is in the electric field produced by a central charge of  $+Ze$ . However, if it is far from the nucleus, the other  $Z-1$  electrons of the atom screen the nucleus, and the electron only sees a charge of  $+e$ . It turns out that as the value of  $\ell$  is increased, the average distance of the electron from the nucleus also increases. Hence, we would expect the energy levels for an atom in a state of large  $\ell$  to be very similar to those of the hydrogen atom.



**Figure 2. Approximate potential energy as a function of distance from the nucleus.**

#### Sodium

Electrons fill the shells of an atom in a certain order. Since the exclusion principle precludes any two electrons in the atom from having the same quantum numbers, it turns out that each “orbital”, or set of quantum numbers  $n$ ,  $\ell$ , and  $m$  can contain two electrons: one spin up and the other spin down. For example, the 1s shell can contain only two electrons because the only possible set of quantum numbers is  $n = 1$ ,  $\ell = 0$ ,  $m = 0$ . Similarly, the 2p shell can hold 6, since we can have,  $n = 2$ ,  $\ell = 1$ ,  $m = -1, 0, 1$  and we have spin up and spin down. From this we find that the shells will fill up in the order given in Table 2.

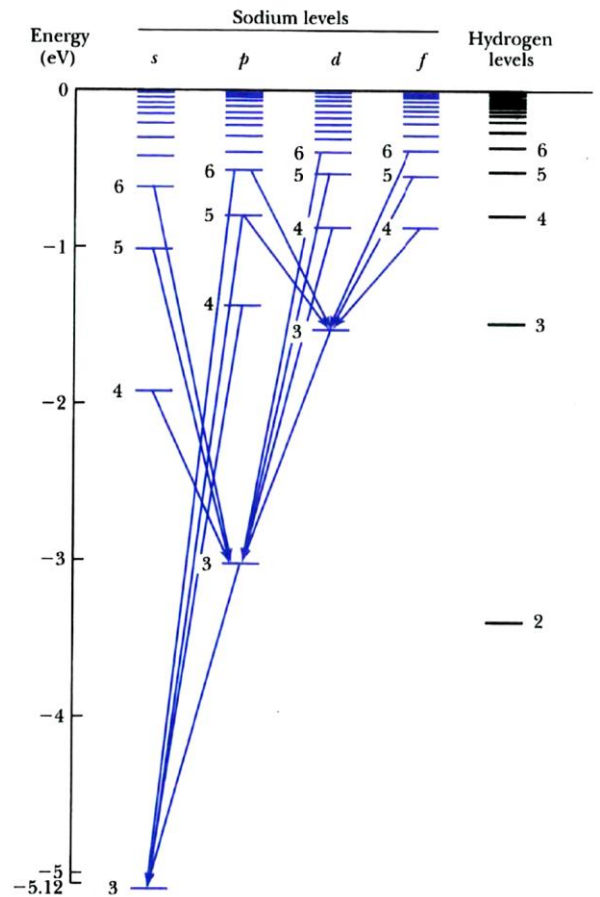
**Table 2. Filling atomic energy levels are filled in multielectron atoms.**

<i>Shell</i>	<i>1s</i>	<i>2s</i>	<i>2p</i>	<i>3s</i>
	$n = 1$	$n = 2$	$n = 2$	$n = 3$
	$\ell = 0$	$\ell = 0$	$\ell = 1$	$\ell = 0$
Element	$m = 0$	$m = 0$	$m = -1,0,1$	$m = 0$
H	1	0	0	0
He	2	0	0	0
Li	2	1	0	0
Be	2	2	0	0
B	2	2	1	0
C	2	2	2	0
N	2	2	3	0
O	2	2	4	0
F	2	2	5	0
Ne	2	2	6	0
Na	2	2	6	1

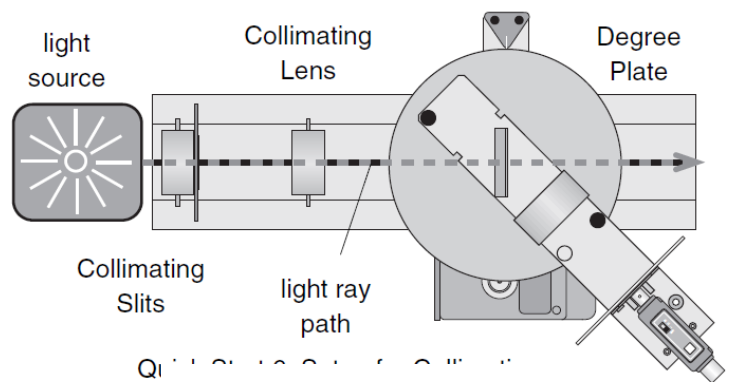
Now, sodium has 11 electrons, so from Table 2 we see that it has one complete closed shell (1s2s2p) and one electron left over in the 3s state. Thus, in some sense it should behave like a hydrogen atom, except for the fact that the central nucleus is “screened” by all of the other electrons. The potential experienced by the 3s electron will be the coulomb potential  $-ke/r$  for large distances from the nucleus, and something like  $-ke/r + C$  up closer. If not for this screening effect, the sodium atom would have the same energy spectrum as hydrogen. As it is, the sodium spectrum looks slightly different, as shown in Figure 4. You can see, however, that it becomes more and more like the hydrogen spectrum at larger and larger values of the orbital angular momentum,  $\ell$ . This makes sense since larger values of  $\ell$  correspond to states where the electron is more likely to be far away, in the region where the potential is most like that for hydrogen.

#### IV. Experimental Apparatus

We will be using discharge tubes as our light source, one for hydrogen, neon and sodium. The light from these tubes will be analyzed by a spectrometer similar to the one used in the previous blackbody



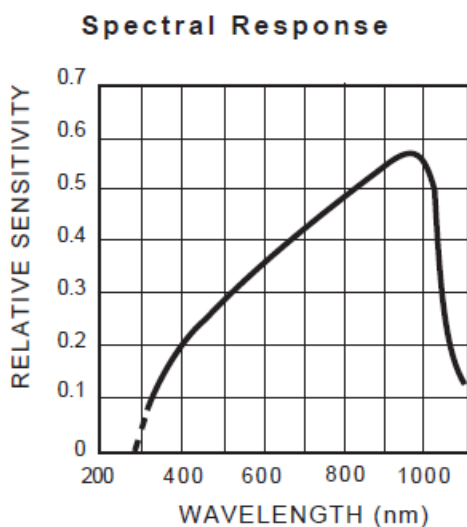
**Figure 3. The energy level diagram for sodium and hydrogen**



**Figure 4. The spectrometer uses a diffraction grating to deflect light. The angle of deflection depends on the wavelength.**

radiation experiment, except that a diffraction grating will be used instead of the prism.

A schematic diagram of the spectrometer is shown in Figure 4. Light from the gas discharge tube is collimated by slits and a collimating lens. It then passes through an approximately 600 lines/mm diffraction grating. Spectral lines are formed at various angles, which are then focused onto another slit. This slit allows the light to enter the Pasco High Sensitivity Light Sensor (CI-6604). The degree plate to which the detector arm is attached may be rotated to sweep through the spectrum. The angle of the degree plate is measured using a Pasco Rotary Motion Sensor (CI-6538).



**Figure 5. The spectral response of the photodiode.**

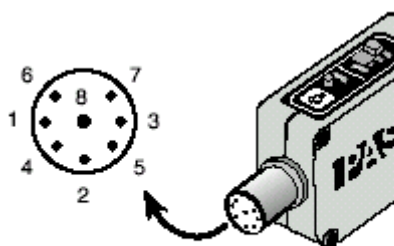
A diffraction grating is a piece of transparent material on which has been ruled a large number of equally spaced parallel lines. The distance between the lines is called the grating line spacing,  $d$ . Light that strikes the transparent material is diffracted by the parallel lines. The diffracted light passes through the grating at all angles relative to the original light path. An image of the light source is formed whenever the diffracted light waves interfere constructively. This will occur whenever the wavelength of the light,  $\lambda$ , the grating line spacing,  $d$ , and diffraction angle,  $\theta$ , have the relationship

$$m\lambda = d \sin \theta, \quad (6)$$

where  $m$  is an integer. The different values of  $m$  result in the grating dispersing the beam of light into a first order spectrum ( $m = 1$ ) and higher order spectra. The higher order spectra are broader and less bright than the first order spectra, and may overlap. The diffraction grating is blazed, so one side of the spectrum is brighter than the other.

The light sensor does not respond equally to all wavelengths. Figure 5 is a plot of the spectral response of the photodiode used in this detector. Clearly, the best results will be obtained in the red part of the spectrum, from 600-1000 nm.

The Pasco Light Sensor is not made to be directly read out into a Vernier interface, so a special connector box was constructed which allows the correct power supply voltages to be connected to the detector, and allows the sensor output to be read as a voltage directly into the Vernier interface. The Vernier interface only accepts voltages in the range of -6 to +6V (using the differential voltage probe), which is acceptable for our application, which usually produces only a few volts. See Table 3 for the proper voltages required to operate the detector.



**Figure 6.** A diagram showing the DIN connector pins of the CI-6628 PASCO infrared sensor.

**Table 3.** The specifications for the DIN connector on the PASCO-6628. The colors indicated are the internal wire colors of the cable.

Pin	Specifications	Color
1	analog output (+), -10 to +10 V	Black
2	analog output (-), signal ground	Brown
3	(no connection)	
4	+ 5 V DC power	Red
5	power ground	Orange
6	+12 VDC power	Yellow
7	-12 VDC power	Green
8	(no connection)	

## V. Experimental Procedure

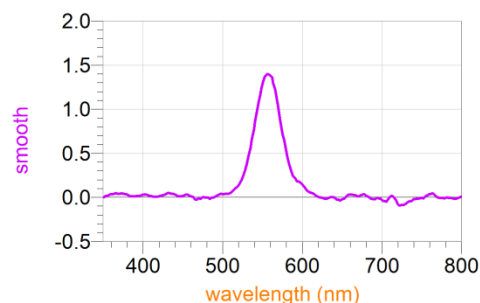
You will be looking at the spectra of four sources: hydrogen, sodium, neon and helium. Please consider the following suggestions.

### Set-up and calibration

- 1. NEVER TOUCH THE SURFACE OF THE DIFFRACTION GRATING! Always handle it by its edge.**
- The focal length of the collimating lens is about 10 cm so the lens should be positioned about 10 cm from the slits. Align a light source so that light from the source passes through a collimating slit and then through the collimating lens onto a distant vertical surface. Adjust the distance between the collimating slits and the collimating lens so that the beam of light is neither converging nor diverging (i.e., light rays are parallel). The light may not be in focus during this process.
- The focusing lens focal length is about 10 cm so the lens should be positioned on the light sensor arm about 10 cm from the front of the aperture disk. Set up the neon light source, which is quite bright, so a beam of light shines through the grating and focusing lens. Darken

the room so you can see the spectral lines more clearly. Move the arm so the central ray of light (called the “zeroth order”) is centered on the aperture slit. You should be able to see the first order spectral lines on the aperture screen on either side of the central ray of light. Move the arm so that the spectral lines are near the aperture slit and adjust the focusing lens until the spectral lines are sharply focused. Because the grating is strongly blazed, the spectral lines on one side of the central ray will be less bright than the spectral lines on the other side. Obviously, use the bright side!

4. Calibrate the angle as measured by the rotation sensor by using the degree plate.
5. Make a column using Equation 6 for the approximate wavelength corresponding to the given angle. The number of lines on the grating is approximately 600 lines per millimeter.
6. Turn on the power supplies for the light sensor. Set the voltages to  $\pm 12$  V as appropriate. The light sensor has settings for  $\times 1/10/100$ . Start with  $\times 100$ . If you discover when you scan a spectrum that this is too much amplification, lower the setting.
7. Use the light emitting diodes (LED) to make a better calibration. Make sure not to allow the current to be higher than the maximum printed on the LED holder for each LED. **Make sure the current limiting resistor is in the circuit or you will burn out the LED.** Do a scan with several LEDs, determine the center of the peak for each LED and make a linear calibration to the known wavelengths printed on the holder. Make another column of the corrected calibration.



**Figure 7. Calibration peak using the 560 nm LED.**

### Measurement #1 – Hydrogen

1. Using Equation 5, predict the wavelengths for hydrogen transitions that fall in the part of the spectrum to which the light sensor is sensitive. Let’s see how this agrees with what we actually measure!
2. Place the hydrogen discharge tube directly in front of the front spectrometer slit. Turn on hydrogen light source. Allow time for it to warm up – the color will change slightly as the tube comes to equilibrium. You may want to use aluminum foil to shield the light source to prevent stray light from entering your light sensor.
3. Align the spectrometer and the light source so that maximum intensity is obtained in the light sensor. Careful -- the discharge tube can get very hot. **Be careful to do nothing that might change the wavelength calibration.**
4. Move the sensor arm to scan through the spectrum.
5. Determine the wavelengths of the spectral lines and their uncertainties.

### Measurement #2 – Sodium

1. Replace the hydrogen discharge tube and power supply with the sodium tube. Be sure to allow time for the sodium tube to warm up. It gives off a pinkish glow when first turned on. Wait until the light looks orange-yellow.
2. Repeat the same process as Measurement #1 to obtain a sodium spectrum. Since sodium has only one valence electron, its spectrum should be “hydrogen-like”. Compare the prediction from Figure 3 with your measurement.

### 3. Measurement #3 – Helium

1. The electron configuration for helium is  $1s^2$ . The helium energy level diagram is shown in Figure 8.
2. Replace the sodium tube and power supply with the helium tube. Be sure to allow time for the helium tube to warm up.
3. Repeat the same process as Measurement #1 to obtain a helium spectrum.
4. How many of the transitions in Figure 8 can you identify? Which are missing?

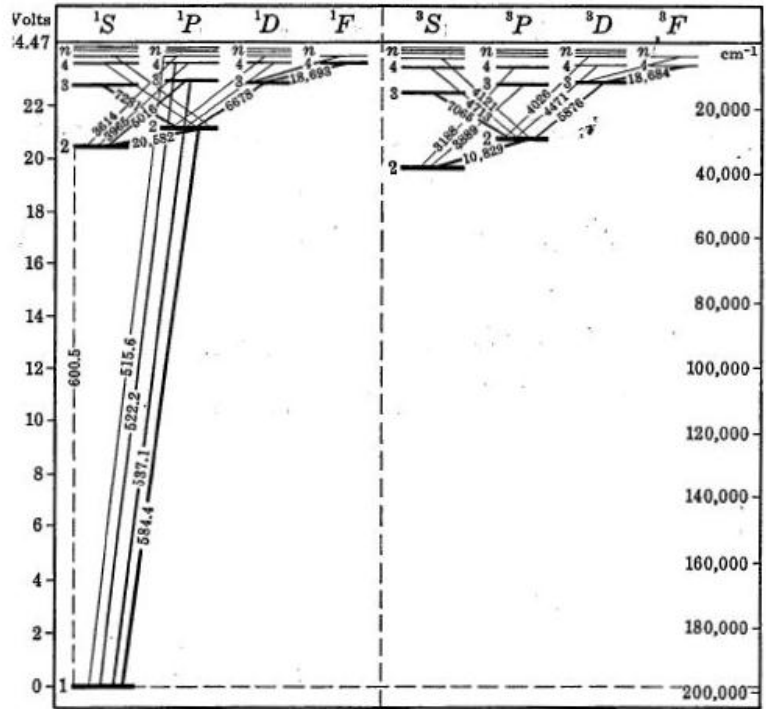


Figure 8. Energy level diagram for Helium. The wavelengths for many transitions are indicated.

### Measurement #4 – Neon

5. The electron configuration for neon is  $1s^2 2s^2 2p^6$ . Make a prediction of what the neon spectrum might look like as compared with hydrogen or sodium.
6. Replace the helium tube with the neon tube. Be sure to allow time for the neon tube to warm up.
7. Repeat the same process as Measurement #1 to obtain a neon spectrum. Does it agree with your prediction?
8. Use <http://www.nist.gov/pml/data/asd.cfm> to examine the spectral lines for Neon. How many are you able to identify in your spectrum? Use the Saha-LTE Spectrum option to predict the neon spectrum. Does it look like your measurement?



## VI. Experimental Results

When you finish the above steps, you should have the following in your logbook (in addition to the usual expectations!)

- 1 Calibration spectra for several LED colors showing best fit to center of the peak.
- 2 Plot of the linear calibration fit.
- 3 Plot of the spectra for hydrogen, sodium, neon and the gas you chose.
- 4 Your predicted transitions for hydrogen and comparison with measurement.
- 5 Comparison of measured sodium lines with prediction from Figure 3.
- 6 Comparison of measured neon lines with Saha-LTE Spectrum.

## V. Questions to ponder:

1. Why is it difficult to detect the hydrogen line at 486 nm? It is easily visible to the naked eye.
2. How close is your rough wavelength calibration to the calibration to known wavelengths? Can you explain why they are different?
3. What is the best width to use for the collimating slit? The aperture slit?
4. Consider the energy levels for hydrogen and sodium. Are all possible transitions allowed? If not, which transitions are allowed? Why are some allowed and not others? Do you see any spectral lines for transitions that are not allowed?
5. Consider Figure 8 showing the energy levels for sodium. Are all possible transitions allowed? If not, which transitions are allowed? Why are some allowed and not others? Do you see any spectral lines for transitions that are not allowed?
6. Describe the neon spectrum. Do you see discrete peaks? Explain.
7. How could the apparatus for this experiment be improved?