Theory

The optical spectra of isolated atoms consist of discrete, unequally spaced lines. This fact could not be understood on the basis of classical atomic models and thus provided one of the points of departure for the development of quantum mechanics. Today the study of atomic spectra is still the principal source of experimental information about the electronic structure of atoms. The spectrum in which one expects to find the simplest regularities is that of hydrogen, the simplest atom. The heavier atoms often have extremely complicated spectra. Nevertheless, certain approximate regularities are prominent, especially in the spectra of those atoms which have only one or two electrons outside of a closed shell.

Certain pairs of lines in one-electron spectra and triples of lines in two-electron spectra are prominent. The yellow doublet of sodium is a well-known example of such a pair, separated by 6 Å. The next element, magnesium, shows triples of lines, also separated by a few Å. These groups can be understood, using the relation

\[ h = E_i - E_f \]

where \( E_i \) and \( E_f \) are the initial and final electronic energies of the atom, as transitions either to or from closely spaced groups of energy levels. In the case of the yellow sodium doublet, the initial states are two 3p states and the final state is the 3s state. In magnesium, a triplet occurs when the initial state is the 4s and the final states are three 3p states.

![Diagram](image)

Figure 1

The splitting of these energy multiplets is due mainly to the so-called spin-orbit interaction.
The splitting can be calculated from the quantum theory of atomic structure. For example, the three p states are found to be separated by Å and 2Å respectively, if certain simplifying assumptions are made ("L-S coupling"). The energy A is rather difficult to calculate. In general, the value of A increases with the atomic number of the atom. The prediction that the separation in energy of one pair of the triplet should be twice that of the other pair is very easy to compare with experiment, however.

In this experiment, the wavelengths of some lines of the zinc spectrum are measured with a precision spectrometer. Three lines of the zinc spectrum between 4000 and 5000 Å belong to the 5s - 4p transitions. In zinc, with atomic number Z = 30, the separation of the lines is greater than for magnesium (Z = 12). The accuracy attainable with the spectrometer used is sufficient to give a critical test of the 2:1 ratio of line separation expected on the assumption of L-S coupling.

Procedure

The apparatus used in this laboratory consists of a gas discharge tube (either sodium, mercury or zinc) with power supply and a grating spectrometer as shown in figure below. The atoms in the discharge tube are excited by means of an electrical current and the light emitted is passed through the diffraction grating of the spectrometer which disperses it into its component wavelengths. The individual lines can be viewed through the observation arm of the spectrometer. Each line can be precisely located using crosshairs in the eye piece of the observation arm. The angle at which the lines appear is read off a scale on the base of the spectrometer.

CAUTION: The power supply produces dangerous voltages. Do not touch the metal.
connectors on the power supply when the power supply is turned on.

The diffraction grating used is a multiple slit system one inch wide with approximately 6000 slits/cm. (The exact value is given on each grating). For any multiple slit system, the angular location $\theta$ of the maxima for light of wavelength $\lambda$ is given by the expression

$$m\lambda = d \sin \theta, \quad m = 0, \pm 1, \pm 2 \ldots$$  \hspace{1cm} (1)

where $d$ is the distance between the slits and $m$ is the order of the maximum. In this experiment, we will be concerned only with the first order spectrum ($m = 1$) which simplifies equation (1) to

$$\lambda = d \sin \theta$$  \hspace{1cm} (2)

Once the angle $\theta$ for a specific spectral line has been measured, with $d$ known for the grating, the wavelength of the line can be computed from equation (2). When the wavelength is known, the energy of the photons producing that line can be calculated and compared to those predicted by theory.

1. Make certain the diffraction grating on the spectrometer is level (using three leveling screws under the grating platform) and is in a plane which is perpendicular (both horizontally and vertically) to the light exiting the arm containing the entrance slits. Do not touch the optical surfaces of the grating. Always handle it by the edges.

Turn on the power supply for the gas discharge tube and turn off the lights in the room. [Note: some of the gas tubes, such as the sodium tube, may take as long as 10 minutes to warm up. You may want to turn them on as soon as you get into the lab.] Position the output port of the discharge tube so that it is just in front of the entrance slit to the spectrometer. Position the observation arm so that it is in line with the arm containing the entrance slit. You should see the bright central maximum in the eyepiece.

The thickness of the line can be changed by opening or closing the entrance slit with the knob next to the entrance slit. Adjust the slit opening until a thin line is obtained. The spectrometer optics can be focused by moving the eyepiece in and out in its holder. Focus the spectrometer so that both the observed line and the crosshairs can be clearly seen. [Note: with some of the spectrometers it may be impossible to have both the line and the crosshairs in perfect focus. In that case, focus them so that the crosshairs are clearly visible and the line is as focused as possible.]

2. Use the following procedure to measure the angular deflection of a line.

   a. Swing the observation arm to one side and set the crosshairs on the spectrum line of
interest. There is a fine position adjustment on the lower part of the observation arm which can be used to accurately position the crosshairs. [Note that the line has a finite thickness and the crosshairs can be placed on either edge or in the middle of the line. Where on the line the crosshairs are positioned does not matter as long as you position the crosshairs in the same way each time you make a measurement (why?).] If the crosshairs cannot be seen, rotate the crosshair illuminator until just enough light is let into the eyepiece so that both the line and the crosshairs become visible. An alternative method of making the crosshairs visible is to shine a flashlight at an angle on the lens where the light from the grating enters the observation arm. If neither of these methods work or if the line is washed out by the increased light, it may be necessary to open the entrance slit a little more.

The angle scale on the base of the spectrometer is divided into two parts, a fixed part containing the degree markings and a movable vernier scale. Each degree on the fixed scale is divided into two parts each representing thirty minutes of a degree. The vernier scale is divided into thirty equal divisions each representing one minute of a degree. A magnifying glass is provided on the spectrometer to assist you in reading the scales. The scales are read in the following way.

1. Determine in which degree division on the fixed scale the zero line on the vernier scale is falling. This gives you the whole degree of the angle being measured.

2. Determine in which half of the degree the zero line on the vernier scale is falling.

3. Determine which line on the vernier scale exactly lines up with a line on the fixed scale. If the zero on the vernier scale is in the first half of the degree, then the minute measurement is simply the value of the line on the vernier scale which lined up with the line on the fixed scale. If the zero on the vernier scale is in the second half of the degree, then the minute measurement is the value of the line on the vernier scale which lined up with the line on the fixed scale plus thirty minutes.

Record the angles to the nearest minute.

Repeat this step for the same line on the other side of the central maximum.

Compute $\theta$ by finding the difference between the two angles and dividing by 2. This method of measuring $\theta$ increases the accuracy the measurement (why?).

3. Measure the wavelengths of the lines of the zinc triplet, using the angles between the first-order images on either side of the zero order image, in conjunction with the known grating spacing. The wavelengths should be checked in higher orders if possible.
4. The experimental resolving power of the grating can be measured if time permits, and the result compared with the limit set by the wave nature of light. Measure the separation of the yellow sodium doublet. Then place a slit in front of the grating, and narrow the slit until the lines are just resolved. The resolution of the partially covered grating is now known; the resolution of the totally illuminated grating is determined as the ratio of the width of the slit to the width of the fully illuminated grating.

5. Other gases are available in the lab which exhibit doublet and triplet lines. Observe some of those gases as time permits.

Lab Report

Follow the usual lab notebook format. Your lab report should include the answers to all of the questions asked in the introduction or procedure, all raw and derived data, and an estimate of the magnitude and sources of error in any data recorded. When answering any question or when giving any comparison or explanation, always refer to specific data to support your statements. For this lab, also do the following.

1. Describe how well the separations of the zinc triplet agree with the 2:1 ratio expected with L-S coupling? What is the value of the coupling constant $A$ for Zn, in eV? For Na? What is the algebraic sign of $A$ for Zn?

2. On the basis of your measurement of the resolving power of this apparatus, discuss the possibility of resolving the spin-orbit triplets in beryllium. Could the hydrogen and deuterium spectra be resolved?