Experiment 7

Study of Atomic Spectra: The Diffraction Grating

1 Introduction

In this experiment, we will employ a plane diffraction grating to create a spectrometer, which we will use to measure a few atomic emission lines of hydrogen (H), sodium (Na) and mercury (Hg). We will use the Hg lines to calibrate the spectrometer. The goals of this experiment are (1) to use the H spectrum to estimate the Rydberg constant and (2) to determine the energy level diagram of the low lying levels of Na and the fine structure splitting of the $3p$ configuration.

2 Theory

2.1 Diffraction Grating

In this experiment, we will use a plane diffraction grating, the large N limit of multiple slits. The diffraction grating therefore produces the same interference-diffraction pattern discussed in Experiment 6. Diffraction gratings can be made by ruling a large number of equidistant lines on a glass substrate. Most gratings today, however, are replicas (molds of ruled gratings).

The maxima produced by a diffraction grating are very sharp. For parallel light incident on a diffraction grating with angle $\theta_i$, the positions of the maxima are given by

$$p\lambda = d (\sin \theta_p + \sin \theta_i), \quad p = \pm 1, \pm 2, \pm 3, \ldots \quad (1)$$

where $p$, $d$, $\theta_p$ and $\theta_i$ are defined in Fig. 7.1 with $p$ designating the order of the spectrum.

It is clear from Eq. (1) that for fixed $p$, the angle $\theta_p$ will be a function of the wavelength of the light. Thus, if we illuminate the
grating with light composed of several wavelengths, each wavelength will emerge with a different angle, i.e., dispersion will occur. Note, however, dispersion only occurs for spectral order greater than zero. At zero order, $\theta_p = 0$, we will see a superposition of all the wavelengths.

The diffraction grating is a particularly simple instrument to use for studying the components of light produced by an excited atom. When the electrons in an atom are excited (have their energy increased), they return to lower states by emitting light of specific wavelengths known as spectral lines. It turns out, that the spectrum of an atom is one of its basic signatures. The existence of many elements in astronomical studies is often established by measurements of their spectra. Atomic spectroscopy has also played a fundamental role in the development of quantum mechanics. Hence, the great theoretical and experimental importance of atomic spectroscopy is well established.

### 2.2 Hydrogen Atom

Bohr’s hypothesis that the electron does not radiate when circling the nucleus, stationary states, allows us to determine the energy spectrum for H. For stationary states to exist, the Coulomb force, $-e^2/4\pi\varepsilon_0 r^2$ (where $e$ is the elementary charge, $\varepsilon_0$ is the vacuum permittivity and $r$ is the radius of the orbit), must equal the centripetal force, $-m_e v^2/r$ (where $v$ is the tangential velocity and $m_e$ the mass of the electron). This leads to a kinetic energy of

$$T = \frac{1}{2} m_e v^2 = \frac{1}{2} \left( \frac{e^2}{4\pi \varepsilon_0 r} \right),$$  \hspace{1cm} (2)

and a total energy of

$$E = T + V = -\frac{1}{2} \left( \frac{e^2}{4\pi \varepsilon_0 r} \right).$$  \hspace{1cm} (3)

As usual, negative energy means the system is bound. Prior to the development of quantum mechanics, it was known that atoms emitted light at specific wavelengths. In the 1889, Rydberg proposed the following formula to describe the frequency of the light emitted when an atom makes a transition between energy levels $n$ and $n'$,

$$\tilde{\nu}_{n'n} = \frac{E_n - E_{n'}}{hc} = \mathcal{R} \left( \frac{1}{n^2} - \frac{1}{n'^2} \right).$$  \hspace{1cm} (4)

In Eq. (4), $\tilde{\nu}(\equiv \nu/c)$ is called the wavenumber – the frequency of the light divided by the speed of light and expressed in units of cm$^{-1}$ – $E_n$ is energy of level $n$, $hc$ is Planck’s constant times the speed of light and the constant $\mathcal{R}$ is the Rydberg constant.
For H, the energy of the \( n^{th} \) level given by

\[
E_n = -\frac{1}{2} \left( \frac{e^2}{4\pi \varepsilon_o n^2 a_o} \right),
\]

where \( a_o \) is the Bohr radius. From Eqs. (4) and (5) it follows that the Rydberg constant for an infinitely massive nucleus is given by

\[
\mathcal{R}_\infty = \frac{1}{2\hbar c} \left( \frac{e^2}{4\pi \varepsilon_o a_o} \right) = \frac{m_e e^4}{4\pi \varepsilon_o \hbar^3},
\]

while the Rydberg constant for an atom of mass \( M \) is given by

\[
\mathcal{R}_M = \mathcal{R}_\infty \left( 1 + \frac{m_e}{m_N} \right)^{-1}.
\]

The energy unit of \( \mathcal{R} \) is most often \( \text{cm}^{-1} \) (wavenumbers) but it is not uncommon to express it in eV as well. Combining Eqs. (4) and (6) leads to the following simple for the H spectrum:

\[
E_n = -\hbar c \mathcal{R}_H \frac{1}{n^2}.
\]

### 2.3 Sodium Atom

The structure of Na is more complicated than that of H because of the presence of 10 additional electrons. Although these electrons are tightly bound in the 1s, 2s and 2p levels, they produce a significant affect on the energy of the outer electron in the 3p level. Qualitatively, the energy spectrum is given by

\[
E_n = -\hbar c \mathcal{R}_{Na} \frac{1}{(n - \mu)^2},
\]

where the principal quantum number, \( n \), is replaced by an effective quantum number with \( \mu \) being the so-called quantum defect. The quantum defect can range in value from \( \sim 0 \) to a significant fraction of the \( n \). Configurations \( (nl) \) with smaller \( l \) values generally experience larger quantum defects. This is because the electron interacts with the other 10 electrons more in these levels. The quantum defect causes the energy levels to shifted relative to what one would expect for H with the same principal quantum number. In addition, the electrostatic interaction between this outer electron and the other 10 electrons leads to a splitting of levels with the same \( n \) and \( l \) but with different \( j \). Note, \( j = l \pm s \). For the 3p level of Na, \( n = 3, l = 1 \) and \( s = 1/2 \) leading to \( j = 1/2 \) and \( 3/2 \).
3 Experiment

3.1 Overview of the Spectrometer

The apparatus used in this experiment is schematically shown in Fig. 7.2. It consists of the plane transmission diffraction grating (~ 600 lines/mm) mounted on the rotating table of the spectrometer. The spectrometer also consists of a telescope and a collimator, both of which can be rotated independently about the axis of the table. A description of each of the numbered parts will now be given.

1. **Table.** Used for mounting a grating or prism.

2. **Eyepiece focus.** At the end of the telescope, this eyepiece can be gently pulled or pushed to get a sharp focus on the cross-hairs without moving their position. This allows the apparatus to allow for different individual viewing preferences without upsetting the focus of the image being viewed.

3. **Telescope focus.** The chrome flange can be rotated to focus the telescope on the image.

4. **Leveling Screws.** These are used to align the collimator and telescope vertically. One screw is a clamp and the other is used for leveling.

5. **Collimator stop.** Adjusts the length of the collimator. The collimator should be set to the correct length when the stop is pushed in against the outer shell. Nevertheless, you may find it necessary to extend the barrel somewhat. If you find that you need to reduce its length, see your instructor.

6. **Collimator** Allows adjustment in width and orientation of the slit.

7. **Telescope arm clamping and tangent screws.** The two screws on the side of the spectrometer just below the telescope each serve a distinct purpose. The screw projecting radially outward is the clamping screw which should always be loosened before attempting to move the telescope. After the telescope is nearly in the desired position, the clamping screw should be gently tightened. The perpendicular tangent screw then allows for very fine adjustment of the telescope position.

8. **Object table clamping and tangent screws.** These adjust the rotating table in the same way as (7) adjusted the position of the telescope arm. They should be used in the same way.
More discussion of the salient features of the spectrometer can be found in the reference manual (see course web page).

3.2 Aligning the Spectrometer

In order to set up the grating on the spectrometer so that we can use Eq. (1), we proceed in the following way.

First, focus the telescope for parallel light (i.e., light from infinity) by focusing on an object several tens of meters away. Focusing through a window on a building across the street will do. Then, minimize the parallax between the focused image and the cross-hairs. That is, locate the image in the plane of the cross-hairs.

Second, put a light source close to the slit of the collimator. Using the telescope, view the slit. Make the slit as narrow as possible. While looking through the telescope, adjust the focus of the collimator so that the image of the slit falls on the plane of the cross-hairs. This is done by removing any parallax between the image of the slit and the cross-hairs. Now the collimator is set to produce a collimated beam, i.e., a parallel beam of light.

Third, mount the grating on the table of the spectrometer. Make sure that the photographic film from which the grating is made is on the telescope side. (The excess glass should protrude towards the telescope side.) Note the position of the telescope when it is in line with the collimator, i.e., when the slit image is aligned with the cross-hairs. Shine the light from your desk lamp into the open side port of the telescope (near the eyepiece) to illuminate the cross-hairs. You might find it helpful to place a mirror just behind and flush with the grating to see the reflected image of the cross-hairs. Once you have located it, you can remove the mirror and continue with the alignment procedure. Rotate the grating so that the reflected image of the cross-hairs falls back on the cross-hairs. In this position, the grating is aligned with the telescope. The system is set up to approximately satisfy Eq. (1); the incident beam consists of parallel light falling nearly normally on the grating, i.e., \( \theta_i = 0 \). Lock the grating into place and record the position of the angular scale on the rotating table. You will be able to see images of successive orders of the spectrum by rotating the telescope away from the zero order position.
3.3 Making Measurements of Various Spectra

As mentioned earlier, the sources you will be observing are mercury, hydrogen, and sodium. You will be able to see first order spectra for all of these light sources. With the room lights out, you will also be able to detect some of the lines in second order.

To make measurements, first record the value of the angular scale on the rotating table when the cross-hairs are aligned with the zero order spectrum (this corresponds to \( \theta_p = 0 \)). Rotate the telescope to the right so that the cross-hairs align with a \( p^{th} \) order spectral line. Record the angular scale reading. Then, rotate the telescope so that the cross-hairs align with the corresponding spectral line on the left side of the zero order spectrum; record the angular scale reading. You should measure the angle for each spectral line at least twice on each side, giving you at least four measurements of the angle, \( \theta_p \) for the \( p^{th} \) order. Take the average as your result and the standard deviation as your uncertainty. This should be done for each visible spectral line. Note, you might find it easier to measure all the lines on one side before measuring them on the other side. With these measurements, you will be able to calculate \( \lambda \), the wavelength of each spectral line.

The scale on the spectrometer is a vernier scale. The outside scale is ruled in 0.5 degree; the inside scale is ruled in minutes of arc. To read the angle, look at 0 on the inner scale. Say it falls between 180.0 and 180.5 on the outer scale. Now look for the point where the outer and inner scales line up. Say it is aligned with 24 on the inner scale. Your angle would be 180° 24'. If the 0 of the inner scale were between 180.5 and 181.0 then your angle would have been 180° 54'. **Always, always, always when making your measurements, rotate the table in the same direction, cw or ccw.**

3.3.1 The Mercury Spectrum

You will use the Hg spectrum as your wavelength standards to calibrate your spectrometer. The wavelengths can be found on the course web page. You should measure the angles of the five lines (violet, blue, blue-green, green and yellow). From the known wavelengths, you can use Eq. (1) to refine your value of \( d \) (\( \sim 1/600 \) mm). Do this by fitting \( \lambda \) to \( d \sin \theta \) and extracting a value for \( d \) from the fit parameters.

3.3.2 The Hydrogen Spectrum

With the hydrogen lamp, measure the wavelengths of the violet, blue and red spectral lines. The wavelengths you measure are the air wave- lengths. To determine the Rydberg constant, you will need vacuum
wavelengths,
\[ \lambda_{\text{vac}} = \frac{2\pi c}{\omega} = \frac{1}{\nu} \quad (10) \]
where \( \omega \) is the angular frequency. Given the air wavelength, the vacuum wavelength can be calculated with
\[ \lambda_{\text{vac}} = n_{\text{air}} \lambda_{\text{air}} \quad (11) \]
where \( n_{\text{air}} \) is the index of refraction of air; its value can be found in the handbook of Physics and Chemistry. You can determine \( R_H \) by fitting \( 1/\lambda_{\text{vac}} \) to
\[ R_H \left( \frac{1}{2^2} - \frac{1}{n^2} \right) \quad (12) \]
Convert \( R_H \) to \( R_\infty \) and compare your estimate with the tabulated value.

3.3.3 The Sodium Spectrum
With the sodium lamp, you should measure the wavelengths of the green, yellow and red spectral lines in first order. Use the table of lines for Na on the course web page to determine the \( nls \) (configurations) associated with each line. Sketch and label an energy level diagram in wavenumber units (cm\(^{-1}\)) for the first four levels. Indicate the energy of each level relative to the ground, 3s level. Set the energy of the ground state to 0 cm\(^{-1}\). Effectively, you have shifted the energies to positive energies. Instead of the ionization limit being located at 0 cm\(^{-1}\), the ground state is located at 0 cm\(^{-1}\). Again, you will need to convert to vacuum wavelengths before determining the energy of the levels. Indicate the transitions you measured by wavy arrows.

You should also be able to measure the yellow Na lines in 2\(^{nd}\) order. Calculate the splitting of the yellow doublet in wavenumbers. Add this splitting as an expanded detail to the right of the position of the 3p level in your diagram.

For Further Reading:


5. Course web page.