Optical Spectroscopy of Hydrogenic Atoms

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This experiment is an exercise in optical spectroscopy and a study of the spectra of hydrogenic atoms: atoms with one "optical" electron outside a closed shell of other electrons. A high-resolution scanning monochromator is used to study the Balmer lines of hydrogen and the more complex hydrogenic spectrum of sodium, using the mercury spectrum as the wavelength calibrator. The measured Balmer wavelengths are compared with the wavelengths predicted by the quantum theory of the hydrogen spectrum, and a value of the Rydberg is derived. The transitions responsible for the sodium spectrum are identified, and regularities in the fine structure and adherence to selection rules are observed. A measurement of the isotope shift between the Balmer lines of hydrogen and deuterium is made from which the ratio of the deuteron mass to the proton mass is derived.

PREPARATORY QUESTIONS

Please visit the Hydrogenic Spectroscopy chapter on the course website to review the background material for this experiment. Answer all questions found in the chapter. Work out the solutions in your laboratory notebook; submit your answers on the course website. [Note: Not available to OCW users]

SAFETY

PERSONAL HEALTH AND SAFETY

- The gas discharge lamps used in this experiment can present an electrocution hazard if misused: touching the electrodes that are exposed when the bulb is removed may expose you to dangerous electric currents. Ensure that the lamp is unplugged before changing the bulb!
- Note that the glass bulb in the gas discharge lamp will become too hot to touch very quickly while in use. Before changing out the bulb, allow it to cool for at least a minute after powering off the lamp and then make sure it is not too hot to touch.
- As you will often be working with the room lights off, familiarize yourself with your physical surroundings so that you can perform tasks safely in the dark, such as exiting the room in case of emergency.
- Some light sources may emit ultraviolet light, such as mercury vapor lamps in which the bulb is made of fused silica (quartz) instead of more common types of glass that do not transmit deep in the UV. Avoid looking directly at such light sources without eye protection, especially while in a darkened room where your pupils will be dilated.

EQUIPMENT SAFETY

- Do not touch the diffraction grating or misalign any optical components inside the monochromator.
- Do not adjust the micrometer that controls the width of either the entrance or exit slit to obtain a separation of less than 3 μ m.
- Ensure that the lid on top of the monochromator housing is fully closed before applying the required +900 VDC bias voltage to the photomultiplier tube.
- Before beginning each scan of the monochromator, double-check that the final counter position of the scan is less than 15000. The motor will mechanically jam if you attempt to drive it past 15000. Also check that the total number of steps in the scan will be less than several thousand, as such scans will take several hours to run.

MEASUREMENT OBJECTIVES

In this experiment you will work toward the following objectives:

- Measurement of the wavelengths of the Balmer lines, verification of the Balmer/Bohr formula, and determination of the Rydberg constant
- Measurement of the isotopic shift in the Balmer lines and determination of the ratio of the mass of the deuteron to the mass of the proton
- Measurement of the doublet separations of the spectral lines of sodium and the identification of the quantum transitions responsible for the lines
- Additional objectives at your discretion.

I. INTRODUCTION

The study of the optical spectra of hydrogen and other atoms having a single "optically active" electron in a spherically symmetric potential was especially important in the development of modern physics because of the simplicity of the spectra and the clarity with which their features could be understood in terms of the developing theories of quantum mechanics, quantum electrodynamics, and atomic structure. The purpose of this experiment is to acquaint you with some of these features and with some of the methods of optical spectroscopy through an investigation of the spectra of hydrogen, deuterium, and the alkali metals.

Bohr's theory of the optical spectrum of hydrogen, published in 1913, opened the door to the modern theory of atomic structure. In 1912 Bohr had come to Rutherford's laboratory at Manchester University where, in the previous year, Rutherford had conceived of the atomic nucleus to explain the observations of the scattering of alpha particles by thin metal foils. Bohr immediately began to wrestle with the problem of how electrons in orbit about a nucleus can constitute a stable system when the classical laws of electromagnetism imply they must radiate their orbital energy and spiral into the nucleus. Bohr concluded that new, non-classical physical principles must govern atomic phenomena. By the summer of 1912 he arrived at his central idea that some form of quantization restricts the orbits of electrons inside atoms. He had in mind the quantum idea introduced by Planck in 1900 in his theory of the spectrum of blackbody radiation and invoked by Einstein in 1905 to explain the photoelectric effect. Then somebody brought to Bohr's attention the simple regularities of the hydrogen spectrum, expressed in the formula discovered by Balmer in 1885. Afterward he said, "As soon as I saw Balmer's formula the whole thing was immediately clear to me" (Rhodes 1986 [1]).

The Balmer spectrum of atomic hydrogen is readily produced by an electrical discharge in molecular hydrogen (H₂) at low pressure. The resulting collisions of mildly energetic electrons with hydrogen molecules cause dissociations of the molecules and excitations of the resulting unbound atoms to states which decay in transitions that yield the Balmer lines in the visible region of the spectrum, as well as the Lyman lines in the ultraviolet, and other series of lines in the infrared. Measurement of the wavelengths of the Balmer lines, verification of the Balmer/Bohr formula, and determination of the Rydberg constant are the first objectives of this experiment.

Interesting variations on the theme of the hydrogen spectrum are found in the spectra of other single-electron atoms such as deuterium, tritium, singly ionized helium, doubly ionized lithium, all the way up to 25-times ionized iron. One expects the spectra of these atoms to be similar to that of hydrogen except for the effects of changes in the reduced mass, the nuclear charge, and the hyperfine interactions between the electronic and nuclear magnetic moments. In the laboratory it is difficult to produce a sufficient density of excited, multiply-ionized helium or lithium to yield a detectable spectrum of their singleelectron ion species. Spectral lines from hydrogen-like iron and other elements with atomic numbers greater than that of lithium have been observed in the radiation from solar flares, supernova remnants, neutron stars in accreting binary systems, the hot intergalactic gas in clusters of galaxies, and other cosmic X-ray sources. Some of these spectral lines have also been studied in the laboratory, but only with highly sophisticated equipment not available in the Junior Lab.

The effect on the spectrum of a change in the reduced mass of the nucleus-electron system is readily observed by comparing the spectra of hydrogen and deuterium. Measurement of this "isotope" shift in the Balmer lines and determination of the ratio of the mass of the deuteron to the mass of the proton is another objective of this experiment.

Another kind of "hydrogenic" spectrum is produced by atoms with one electron outside of "closed" shells. Examples are the spectra of the alkali metals, singlyionized alkaline earth metals, doubly-ionized elements in the third column of the periodic chart, etc. In such an atom or ion a single "optical" electron moves in the spherically symmetric potential of the nucleus and the closed shells of the inner electrons, and the eigenstates and energy eigenvalues of the atom can be calculated, in principle, as perturbed solutions of the Schrödinger equation for a hydrogen-like atom with a perturbation potential that represents the distortion of the simple 1/r potential of a point nucleus by the inner electrons. One effect of this shielding is to enhance the splitting of the levels with angular momentum quantum numbers L > 0due to the spin-orbit interaction. Measurements of the doublet separations provide clues to the identity of the states involved in the transitions that give rise to the lines. A third objective of this experiment is the measurement of the doublet separations of the spectral lines of sodium and the identification of the quantum transitions responsible for the lines.

Most of the theoretical background you need for understanding the atomic spectra to be measured in this experiment may be found in the appendices and in Melissinos (2003) [2]. More thorough treatments can be found in your texts for 8.04 and 8.05, e.g. [3, 4]. Another useful and classic reference is *Introduction to Atomic Spectra* by C. F. White (1934) [5]. Here we will concentrate on describing the features of the equipment and procedures peculiar to the setups in Junior Lab. Excellent discussions of the optics of monochromators and spectrometers is given in Jobin Yvon's Tutorial *The Optics of Spectroscopy* by J.M. Lerner and A. Thevenon [6] and, more rigorously, in *Optics* by E. Hecht (2002) [7].

To follow the discussion of atomic structure in the references and to be able to adequately describe the results of your experiment, it will be useful to understand spectroscopic notation: the upper left superscript is equal to 2s + 1, the main symbol corresponds to l, and the lower right subscript is the total angular momentum j. For example, ${}^{2}P_{3/2}$ is the state s = 1/2 (2s + 1 = 2), l = 1 (P), j = 3/2.

II. EXPERIMENTAL APPARATUS

The instrument used to perform this experiment is a research grade high-resolution scanning monochromator (Jobin Yvon 1250M, see the schematic diagram in Fig. 1). The spectral resolution achieved by this monochromator depends on the entrance and exit slit widths, the line spacing of the grating, the degree to which the grating is fully illuminated, and the wavelength of the radiation being studied. When these factors are chosen judiciously, the resolving capacity $R_{max} = \lambda/\Delta\lambda$ may exceed 10^5 .

The monochromator has been painstakingly aligned. Please do not alter the arrangement of the optical components between the entrance and exit slits, i.e., inside the enclosure. You may adjust the other parts of the equipment, *i.e.*, the slits themselves and external optics which couple the light source to the entrance slit. If you suspect misalignment of the internal parts of the monochromator, ask for help.

The monochromator utilizes what is known as a Czerny-Turner mount. In this configuration, light from a source shines — perhaps with focusing — on an input aperture, or entrance slit, through which it illuminates a concave spherical mirror. The mirror is located a distance from the slit equal to the focal length of the instrument. The mirror collimates the diverging light rays from the slit to a make a beam with planar wavefronts. This beam is directed toward a plane reflection grating which can be reoriented by a precision stepping motor. Some of the light reflected (and dispersed) from the grating is intercepted by a second spherical concave mirror which refocuses the light, ideally in the plane of an exit slit. The photons that pass through this slit are detected and integrated using a photomultiplier tube (PMT). The monochromator is interfaced via a GPIB connection to a desktop computer running Microsoft WINDOWS and National Instruments LABVIEW software.

The basic steps for using the instrument are as follows:

- 1. Note the position of the grating's mechanical counter on the side of the monochromator. If it is not close to zero, please seek help from the technical staff. At the end of your session, return the monochromator's grating to the zero position before shutting off the motor controller unit. Failure to do so will frustrate the calibration of the next group.
- 2. Turn on the mercury discharge lamp and place it so that its emission falls upon the entrance slit. If you need to change the bulb in the lamp, unplug it first. Do not touch the electrodes of the lamp. Be aware that the bulb may be hot if the lamp was recently used.

has a blaze wavelength of 400 nm while the grating in position "1" has 3600 grooves/mm with a blaze wavelength of 300 nm. (The unit grooves/mm may be abbreviated lpmm for "lines per millimeter".) **Do not touch the delicate gratings.**

The turret and gratings are rotated by a springloaded lever set against the grating mount which is attached to a turret inside the instrument. Please do not attempt to change the turret yourself since a slip may damage the very expensive gratings.

It is recommended that you start with the coarse 1800 lpmm grating in order to survey the broadest portion of the spectrum and explore the operation of the instrument before making your final measurements.

- 4. Replace the lid with 4 screws above the turret grating assembly.
- 5. Turn on the Ministep Driver Unit (MSD-2) using the power switch on the back panel. You should hear a small clunk as the gear motor is engaged. Power cycling once or twice is sometimes necessary.
- 6. The LABVIEW monochromator control program user interface display is shown in Fig. 2. After the program is loaded, run the code by clicking on the white arrow in the upper left corner of the window. The main drop down menu bar contains various operations for controlling the monochromator.
- 7. Select the desired grating ("1800 lpmm" or "3600 lpmm") and then "Change Turret Position" from the drop down menu bar. Wait for the menu bar to revert back to "Waiting for next command" before proceeding. You should execute this step even if the display reads the correct position, as it needs to retrieve information about the grating's groove density.
- 8. Examine the mechanical counter on the side of the monochromator to see that it reads exactly 0.0. If not, select "Move grating to zero position" from the menu bar. This counter can be used to determine the current wavelength setting according to $\lambda = \text{counter} \times \frac{1200 \text{ lpmm}}{X \text{ (lpmm)}}$ where X is either 1800 or 3600 depending on the grating in use.
- 9. Due to technical issues, a dummy scan must be performed before the PMT can be biased. Tell the monochromator to perform a short scan over a ~ 1 Å range and select "SCAN MONOCHROMATOR" from the drop down menu bar. Now the PMT

voltage can be set. Double check that the top of the monochromator is covered before turning on the high voltage to the photomultiplier tube as ambient light levels can damage a PMT biased at high voltages. Set the high voltage to +900 VDC.

- 10. The entrance and exit slit widths are controlled by micrometers. They can be set from 3 μ m to 3 mm. Set the width of each slit initially to be 100 μ m. Do not attempt to adjust the micrometers to set either the entrance or exit slit width to less than 3 μ m. This can damage the blades that precisely define the openings! (If you do not know how to read a micrometer dial, please ask for help.) The height of the entrance slit is controlled by another sliding blade and should be set initially at 2 mm.
- 11. The light "acceptance cone" of the instrument is set by the size of the grating $(110 \times 100 \text{ mm})$ and the focal length of the first spherical mirror (1250 mm). For this instrument, the F# — *i.e.*, the ratio of the focal length to mirror diameter — is 11. If you find that you are photon limited, try using a short focal length lens to form an image of the lamp at the entrance slit. This should be F#-matched to the monochromator so as not to underfill or overfill the first spherical mirror. It should also be noted here that the spectral resolution may be degraded if the grating is not fully illuminated.

The wavelength range of the monochromator is 0-15,000 units as displayed by the mechanical counter. Without calibration corrections, the counter gives only a rough value for the wavelength. However, the counter will serve as the basis for wavelength calibration. (See below.)

III. MEASUREMENTS

III.1. Wavelength Calibration

Your first task is to examine the instrument's wavelength calibration. Measure several lines in the mercury spectrum (using the CRC handbooks or the NIST web site for reference data) and make a graph of wavelength *vs.* mechanical counter reading.

Explore the effects of entrance and exit slit widths, entrance slit illumination configuration, grating line density, and integration time on spectral intensity, spectral resolution, and spectral bandpass. The acquired spectrum will probably show a profusion of lines: many more than the prominent yellow, green, blue and purple lines of the famous mercury spectrum. Some of the lines may be ultraviolet lines in the second-order spectrum, superimposed on the visible lines of the first-order spectrum. (An ordinary glass slide placed between the lamp and the entrance slit should be sufficient if you wish to explore the effects on the spectrum of blocking any potential ultraviolet emission from the mercury vapor.) Your first job is to identify as many lines as possible with the aid of the mercury spectrum table in the CRC handbook or on the NIST web site. Later, you will use the mercury spectrum as your calibration for measurements of the hydrogen and sodium spectra.

As noted above, even though the mechanical counter of the monochromator only gives the wavelength rather approximately, it still may serve as a basis for wavelength calibration. The goal of the calibration procedure is to obtain a functional relation between wavelength and the mechanical counter value. With the establishment of an accurate relation for each spectral order, the mechanical counter value may be converted to a relatively accurate wavelength that applies to that order.

Identify the mercury spectral lines by means of a bootstrap operation in which you first latch onto several of the most prominent lines, establish a tentative wavelengthcounter relation, and then see if the other fainter lines fall in place. The yellow doublet (5789.7 Å and 5769.6 Å), the green line (5460.74 Å) and the purple line (4358.33 Å) are particularly useful landmarks within the mercury spectrum. It will help to make a plot of wavelength versus counter value. Look out for second order UV lines superposed on the first order visible spectrum. For example, a 2500 Å line in second order would fall at exactly the same position as a 5000 Å line in first order).

Label as many of the transitions as you can with the aid of Figure 1.24 of Melissinos¹. Note in particular the lines due to the interesting transitions $6^3D \rightarrow 6^1P$ for which $\Delta s = 1$. Also note the 2536.5 Å line which is due to the decay of the first excited state and which is involved in the Franck-Hertz experiment. Check the validity of the dipole radiation selection rules.

Few mercury lines will be seen in the red part of the spectrum. It may therefore be useful, as an optional activity, to use lines of neon to extend the basis for your calibration to longer wavelengths. Ideally, the lines used for your wavelength calibration should span a larger region in terms of wavelength than the hydrogen or sodium lines to be investigated, so that later application of your calibration involves interpolation rather than extrapolation.

After you obtain a set of wavelength-counter pairs of values that span a wide wavelength range, find a function of the counter value that gives an accurate value for wavelength. You may also want to consider the implications of obtaining spectra with an instrument that is immersed in air and is not in an evacuated enclosure.

Make sure to note all instrument settings used when obtaining calibration data. It is best to use the same settings when obtaining hydrogen and sodium spectral

¹ Note: In the first edition of Melissinos, this is Figure 2.13 and the figure caption contains a typo: "hydrogen" should be "mercury".



FIG. 1. Schematic of the Jobin Yvon 1250M monochromator.

data. It may also be worthwhile to check the calibration at the beginning of each lab session.

III.2. Hydrogen Spectrum: The Balmer Series

The goals of this part of the experiment are:

- 1. to record the hydrogen spectrum;
- 2. to identify the Balmer lines and measure their

wavelengths using a wavelength calibration;

3. to compare the measured wavelengths with the Balmer formula, namely

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right),\tag{1}$$

where $n_i > n_f$ are integers, $n_f = 2$ corresponds to the Balmer series in the visible, and $n_f = 1$ corresponds to the Lyman series in the ultraviolet; and



FIG. 2. The LABVIEW software interface to the Jobin-Yvon 1250M monochromator. Note that the user should always enter spectral units of Å while the "counter" indicator will display the mechanical counter positions necessary to scan this portion of the spectrum. The limits of the instrument are 0 to 15,000 in mechanical counter units. Be very careful not to drive the grating beyond this limit!

4. to determine the value of the Rydberg constant, $R_H = \frac{M}{M+m} R_{\infty} = 1.096776 \times 10^7 \text{ m}^{-1}.$

Acquire a series of hydrogen spectra experimenting with resolution changes and integration times. Identify and measure as many of the Balmer lines as you can, comparing the wavelengths with those predicted by Equation (1). You should also use your measured Balmer line wavelengths, together with appropriate values of n_f and n_i , to determine a value and error for the Rydberg constant.

You will probably observe other fainter features in the spectrum of the hydrogen discharge tube. Try to identify them.

III.3. Sodium Spectrum: Fine Structure

The goals of this part of the experiment are:

- 1. to obtain a calibrated spectrum of sodium;
- 2. to measure the wavelengths of the lines and to measure their doublet separations;
- 3. to identify the transitions that give rise to the observed lines; and
- 4. to determine the maximum energy of excitation of the sodium in the lamp.

The distortion of the 1/r field of the nucleus by the inner electrons has a substantial effect on the fine structure splittings of the l > 0 states that arise from the interaction between the magnetic moments associated with the spin and orbital angular moments of the optical electron. While the fine structure splitting in hydrogen is very small and difficult to detect (0.08 Å in H_{β}), it is readily observed and measured in the alkali atoms. The level splitting decreases with n and l approximately as $1/[n^3l(l+1)]$. The splitting of the levels gives rise to a corresponding "doublet" structure of the spectral lines, with the most conspicuous effects occurring in the lines due to transitions to and from the P (l = 1) states. Doublets due to transitions that begin or end at a common state have identical energy separations. In the early days of quantum mechanics, these separations provided important clues for identifying the transitions and deducing the energy levels from observed spectra. See Melissinos for an energy level diagram for sodium.

Obtain sodium spectra of varying integration times both with and without the ultraviolet filter. Determine the wavelengths of all the features of the spectrum.

Identify as many of the sodium lines as you can together with the initial and final atomic states of the transitions. Group them according to common final states and within each group compare the wavelengths with those expected from energy levels given by the Rydberg formula

$$E_m = E_\infty - \frac{hcR}{(m+\mu)^2},\tag{2}$$

where m is an integer, and E_{∞} and μ are constants.

Determine the fine-structure splittings of the ${}^{2}P$ levels involved in the transitions responsible for the various doublets. Check whether the doublets originating from and terminating at the same ${}^{2}P$ level have the same separation in terms of wave number. Determine the ratio of the doublet separations of the 3P and 4P levels, and compare with the semi-empirical rule that the ratio is proportional to $1/n^{3}$. Approach these measurements as an exercise in experimental accuracy and error estimation, and their interpretation as a challenge to your understanding of atomic structure.

You may find there are lines you cannot identify using only the sodium lines listed in the CRC Tables. Try to identify them, *i.e.*, figure out what other element(s) may be in the lamp.

III.4. Measuring Isotopic Shifts in the Balmer Lines

In this part of the experiment you will determine the ratio of the deuteron mass to the proton mass by mea-

- [1] R. Rhodes, *The Making of the Atomic Bomb* (Simon and Schuster, 1986).
- [2] A. Melissinos, *Experiments in Modern Physics*, 2nd ed. (Academic Press, 2003).
- [3] A.P.French and E. Taylor, An Introduction to Quantum Physics (Norton, 1978).
- [4] S. Gasiorowicz, Quantum Physics, 2nd ed. (Wiley, 1996).
- [5] C. White, *Introduction to Atomic Spectra* (McGraw-Hill, 1934).
- [6] J. Lerner and A. Thevenon, *The Optics of Spectroscopy* (Jobin-Yvon, 2000).

suring the isotope shifts of the Balmer lines. Most of the differences in the energy levels of the hydrogen isotopes (hydrogen, deuterium, and tritium) arise from the differences in the reduced mass that occurs in the simple Bohr theory that explains the Balmer formula. (The differences due to interactions involving the nuclear magnetic moments are much smaller in magnitude and not detectable with our instruments). With a little algebra, the ratio of the deuteron mass to the proton mass can be expressed in terms of the wavelength λ of a Balmer line and its shift $\Delta \lambda$ between hydrogen and deuterium.

IV. ANALYSIS

Identify the wavelength (and uncertainty estimate) of each spectral peak in instrument units (proportional to mechanical counter values). Use the best-fit calibration model that you obtained from analyzing the mercury spectrum to interpolate these measured values to obtain more accurate wavelengths, propagating errors from both the measurements and the uncertainties in the bestfit calibration. From these calibrated wavelength measurements, compute the Rydberg constant according to Equation (1). Compute the fine structure splitting in sodium. Compute the value of m_D/m_P and estimate its uncertainty from the measured (and calibrated) wavelengths of the hydrogen and deuterium Balmer lines. Compare the results with the known ratio of the atomic weights of deuterium and hydrogen.

POSSIBLE THEORETICAL TOPICS

- 1. Derivation of the grating equation
- 2. Bohr theory of the hydrogen atom and the isotope shift
- 3. Schrödinger theory of the hydrogen atom
- 4. Fine structure
- 5. The correspondence principle
- [7] E. Hecht, *Optics* (Addison Wesley, 2002).



FIG. 3. Reflection grating geometry. (a) A beam of monochromatic light of wavelength λ is incident on a grating and diffracted along several discrete paths. (b) For planar wavefronts, the terms in the path difference, $d \sin \alpha$ and $d \sin \beta$, are shown. (From Thermo RGL Handbook.)

Appendix A: Grating Physics

Fig. 1 shows the optical layout in the monochromator. Note that the "source" for this system is a narrow slit which is, in turn, illuminated by an external light source. To understand the optics of any spectrograph or monochromator it is essential to realize that a narrow spectral "line" is actually a monochromatic image of the entrance slit. Widen or lengthen the slit and you widen or lengthen the resulting spectral line. The width of a line depends on the width of the slit, the sharpness of the focus, the intrinsic spectral width of the line, and the number of reflecting grooves of the grating that contribute to the total amplitude of the optical disturbance at the focal plane.

To understand the physics of a monochromator, envision spherical monochromatic light waves (*i.e.*, "Huygens wavelets") diverging from any given point at the slit and which are reflected by the collimating mirror into plane waves traveling toward the plane reflection grating. Reflections from the grooves in the gratings form cylindrical wavelets which interfere constructively only in certain narrow ranges of directions so as to comprise, in effect, a set of plane waves each traveling in one of those directions.

A second mirror focuses the incident plane waves to form a diffracted image of the entrance slit at the focal plane of the monochromator. In the focal plane, the spectrum appears as monochromatic slit images spread out in the direction of dispersion of the grating. The position of the spectrum in the focal plane is adjusted by rotating the grating about a vertical axis. The focused light, or some portion thereof, will pass through the exit slit that is ideally located in the focal plane and onto the photocathode of a sensitive photomultiplier tube.

The most general form of the plane reflection grating is shown in Fig. 3. Each "tread" or "riser" of the staircase reflects a narrow rectangular piece of an incident plane wave. This piece then spreads about the specular reflection direction according to the principles of Fraunhofer diffraction. The resulting cylindrical wavelets may be thought of as combining at some distance to form diffracted plane waves with maximum intensities in directions such that the difference in path length along the reflected rays from successive grooves is an integer number of wavelengths. This condition is expressed by the grating equation

$$m\lambda = d(\sin\alpha + \sin\beta),\tag{A1}$$

where α and β are the angles between the grating normal and the directions of incidence and reflection, respectively, d is the distance between grooves, and m is an integer called the "order" of the interference.

It is important to note that Equation (A1) implicitly requires the positive sense for each of the angles α and β to be defined in the same direction with respect to the normal to the plane that defines the overall average grating surface. One must be cognizant of the signs of the angles when using this equation. For example, in the right-hand panel of Fig. 3, α and β as shown have opposite signs.

For the Czerny-Turner configuration of the monochromator, the angle between the directions of propagation of the light incident upon the grating and the light leaving the grating that will be focused on the exit slit is more or less constant with a value that shall be denoted by $2\phi_{sep}$. With this definition, we have

$$\beta = \alpha - 2\phi_{sep}.\tag{A2}$$

The angular dispersion produced by this grating is defined by the differential relation

$$\frac{d\beta}{d\lambda} = \frac{1}{d\lambda/d\beta} = \frac{m}{d\cos\beta} = \frac{\sin\alpha + \sin\beta}{\lambda\cos\beta}.$$
 (A3)

For a given diffracted wavelength λ in order m (corresponding to an angle of diffraction β), it is convenient to characterize the *reciprocal linear dispersion* or *plate factor* P, usually measured in nm/mm:

$$P = \frac{d\cos\beta}{mf},\tag{A4}$$

where f is the effective focal length of the instrument. It is a useful exercise to calculate and plot P as a function of wavelength for the grating spacing and geometry of the monochromator used in this experiment.

The gratings used in the Hydrogenic Spectroscopy experiment are ruled with 1800 or 3600 lines per millimeter $(d=5555 \text{ \AA or } 2778 \text{ \AA})$.

Finally, the difference between two wavelengths diffracted at the same angle in successive orders, called the *free spectral range*, gives an indication of the overlap of those orders in the output spectrum. Let λ be the wavelength at any given output angle in spectral order m+1, and $\lambda + \Delta \lambda$ be the wavelength at the same output angle in order m. These wavelengths are related by

$$(m+1)\lambda = m(\lambda + \Delta\lambda) \tag{A5}$$

from which one finds

$$\lambda_{FSR} = \Delta \lambda = \frac{\lambda}{m},\tag{A6}$$

where λ_{FSR} is the free spectral range.

Appendix B: Equipment List

Item	Model	Contact
1" ultraviolet Filter	6057	oriel.com
1" plano-convex Lenses	Various	thorlabs.com
Monochromator	1250M	www.horiba.com
Photomultiplier Tube	R928	hamamatsu.com
H-D Spectral Lamps	Custom	electrotechnical product.co
Spectral Lamps	Various	edmundscientific.com
Labview		ni.com

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