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Optical Spectroscopy of Hydrogenic Atoms

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This experiment is an exercise in optical spectroscopy in a study of the spectra of “hydrogenic” atoms, i.e. atoms with one “optical” electron outside a closed shell of other electrons. Measurement of the Balmer lines of atomic hydrogen and the fine structure of sodium lines; determination of the mass of the deuteron from the isotope shift. 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 quantum theory of the hydrogen spectrum, and a value of the Rydberg is derived. The transitions responsible for the sodium spectrum are identified, and the regularities in the fine structure and adherence to the 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.

1. PREPARATORY QUESTIONS

1. Construct as complete an energy level diagram of atomic hydrogen as you can, and show the transitions that give rise to the Balmer lines. (Incidentally, just exactly what is a spectral “line”?)
2. Define the following terms and, where applicable, calculate them for the two optical systems used in this experiment: *grating equation, diffraction orders, angular dispersion, linear dispersion, resolving power, spectral resolution, bandpass, focal length, f/#, and free-spectral range.* (See [1, 2])
3. Suppose perfectly monochromatic light of wavelength 4500 \AA enters a Czerny-Turner monochromator with the input slit width set at $10.0 \mu\text{m}$, and suppose the beam fully illuminates the concave grating which is a $10 \text{ cm} \times 10 \text{ cm}$ square with $3600 \text{ lines mm}^{-1}$. Make a plot with properly scaled axes of the light intensity versus angular displacement in the focal plane of the spectrograph in the first order diffracted image of the slit. Show quantitatively the salient features of the multiple slit diffraction pattern. (see [2])
4. Throughout this experiment the tabulated wavelengths of the mercury spectrum will be used as the calibration reference. Suppose, however, you had to start from scratch with no reference wavelengths. How would you establish an absolute scale of wavelengths?
5. Predict the isotope shift in wavelength (i.e., the difference in wavelength $\Delta\lambda = \lambda_H - \lambda_D$) of the first 3 Balmer lines of hydrogen and deuterium. (see [3])

2. INTRODUCTION

The study of the optical spectra of hydrogen and other atoms having a single “optically active” electron in a spherically symmetric potential was specially 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 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 the concept of the atomic nucleus had been invented the previous year by Rutherford in his theory 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 [4]).

The Balmer spectrum of atomic hydrogen is readily produced by an electrical discharge in molecular hydrogen (H_2) at low pressure. The resulting collisions of mildly energetic electrons with hydrogen molecules cause dissociations of the molecules and excitations of the resulting 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 Balmer lines, verification of the Balmer/Bohr formula for their wavelengths, 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 single-electron ion species. As for hydrogen-like iron, it has only been seen in the radiation from solar flares, neutron stars in accreting binary systems, and the hot intergalactic gas in clusters of galaxies. But the effect on the spectrum of a change in the reduced mass of the nucleus-electron system is readily observed in 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 alkali metals, singly-ionized 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 $L > 0$ due 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 is the Appendices and in Melissinos (2003) [5]. More thorough treatments can be found in your texts for 8.04 and 8.05, e.g. [3, 6]. Another useful and classic reference is *Introduction to Atomic Spectra* by C. F. White (1934) [7]. 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 [1] and, more rigorously, in *Optics* by E. Hecht (2002) [2]

3. EXPERIMENTAL APPARATUS

The instrument used to perform this experiment is the research grade high-resolution (0.03\AA) scanning **monochromator** (Jobin Yvon 1250M) shown in Fig. 2 which has a maximum resolving capacity $R_{max} = \lambda/\Delta\lambda \approx 10^4$.

The monochromator has been painstakingly aligned. Please do not alter the arrangement of the optical components between the entrance and exit slits. You may adjust the other parts of the equipment, i.e. the slits themselves and the input optics which couple the light source to the input 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 is focused onto an input slit through which it expands to fill a concave spherical mirror at a distance equal to the focal length of the instrument. The collimated light then is reflected onto a plane reflection grating which can be rotated by a precision stepping motor. Light reflected (and dispersed) from the grating is sent to a second spherical concave mirror which refocuses the light in the focal plane of the exit aperture where the photons are detected and integrated using a photomultiplier tube.

4. HIGH-RESOLUTION MONOCHROMATOR

The monochromator is interfaced to a PC running Microsoft Windows and National Instruments LabVIEW software over a GPIB connection. A schematic of the instrument is shown in Figure 2.

The basic steps for using the instrument follow:

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 input slit.
3. Remove the small lid on the top of the monochromator to verify groove density of the installed gratings. The turret holds two gratings, either of which may be selected in software: Grating position ‘0’ has $1800 \text{ grooves mm}^{-1}$ at a blaze wavelength of

400nm while grating position ‘1’ has 3600 grooves mm^{-1} with a blaze wavelength of 300nm.

It is recommended that you start with the coarse 1800 groove mm^{-1} grating in order to survey the broadest portion of the spectrum and explore the operation of the instrument before making your final measurements.

4. 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.
5. The LabVIEW monochromator control program is shown in Figure 1. 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.
6. 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. The two gratings installed on the turret have groove densities of 1800 and 3600 gpm.
7. Examine the mechanical counter on the side of the monochromator to see that it reads exactly 0.0. This counter can be used to determine the current wavelength setting according to $\lambda = \text{counter} \times \frac{X(\text{lpmm})}{1200(\text{lpmm})}$ where X is either 1800 or 3600 depending on the position the grating turret. If not, select ‘Move grating to zero position’ from the menu bar.
8. Replace the lid with 4 screws above the turret grating assembly.
9. **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 +950 VDC.
10. The input and output slits are controlled by micrometers. They can be set from $3\ \mu\text{m}$ to 3mm. Set the width of both slits initially to be $100\ \mu\text{m}$. **Do not attempt to adjust the micrometers to a width $< 3\ \mu\text{m}$. This can damage the sensitive slits!** The height of the input slit is controlled by a sliding blade and should be set initially at 2mm.
11. The light ‘acceptance cone’ of the instrument is set by the size of the grating (110x100mm) and the focal length of the first spherical mirror (1250mm). For this instrument, the $F\# = 11$. 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 which is its $F\#$ matched to the monochromator (so as not to underfill or overfill the first spherical mirror).

The wavelength range of the monochromator is 0-15,000 units as displayed by the mechanical counter. The gratings are rotated by a spring-loaded lever set against the grating mount which is attached to a turret inside the instrument. **Please do not attempt to change the turrets yourself, since a slip may damage the very expensive gratings.**

4.1. MERCURY CALIBRATION SPECTRUM

Your first task is to examine the instruments’ calibration. Measure several lines in the mercury spectrum (using the CRC handbooks for reference data) and make a graph of wavelength vs. mechanical counter reading.

Explore the effects of input and output slit widths, grating line density, and integration time on spectral intensity, spectral resolution, and spectral bandpass. There is a LabVIEW program ‘Model Instrumental Profile’ in the same library as the main control program which can be used to model the effect of different slit widths. 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. Several of the lines are, in fact, ultraviolet lines in the second-order spectrum, superimposed on the visible lines of the first-order spectrum. Your first job is to identify all the lines with the aid of the mercury spectrum table in the CRC handbook. Later you will use the mercury spectrum as your calibration for measurements of the hydrogen and sodium spectra.

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

Label as many of the transitions as you can with the aid of Figure 2.13 of Melissinos (in the figure caption “hydrogen” should be “mercury”). Note in particular the lines due to the interesting transitions $6^3D \rightarrow 6^1P$ for which $\Delta S=1$, and the $2536.5\ \text{\AA}$ line which is due to decay of the first excited state that is involved in the Franck-Hertz experiment. Check the validity of the dipole radiation selection rules.

Determine the number of lines mm^{-1} in the grating by measuring the linear separation of two identified lines of

The screenshot "LabVIEW software interface to the Jobin-Yvon 1250 monochromator" was removed due to copyright restrictions. Reference: <http://www.ni.com/labview/>.

FIG. 1: 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!**

known wavelength on the acquired spectrum and applying the grating equation (see Appendix A).

4.2. HYDROGEN SPECTRUM – THE BALMER SERIES

The goals of this part of the experiment are:

1. to record the hydrogen spectrum at low and high resolutions together with a mercury calibration spectrum;
2. to identify and measure the wavelengths of the Balmer lines using a calibration based on mercury;
3. to compare the measured wavelengths with the Balmer formula, namely

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

where $n_f = 1, 2, 3, \dots$ and $n_i > n_f$. $n_f = 2$ corresponds to the Balmer series in the visible while $n_f = 1$ corresponds to the Lyman series in the UV.

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

Acquire a series of hydrogen spectra with superimposed mercury calibration spectra, experimenting with resolution changes and integration times. Take care not to disturb the instrument between the hydrogen exposure and the mercury calibration exposure. Identify and measure as many of the Balmer lines as you can, comparing the wavelengths with those predicted by Equation 1. One way to do this is to compute a value of λ_0 for each of your

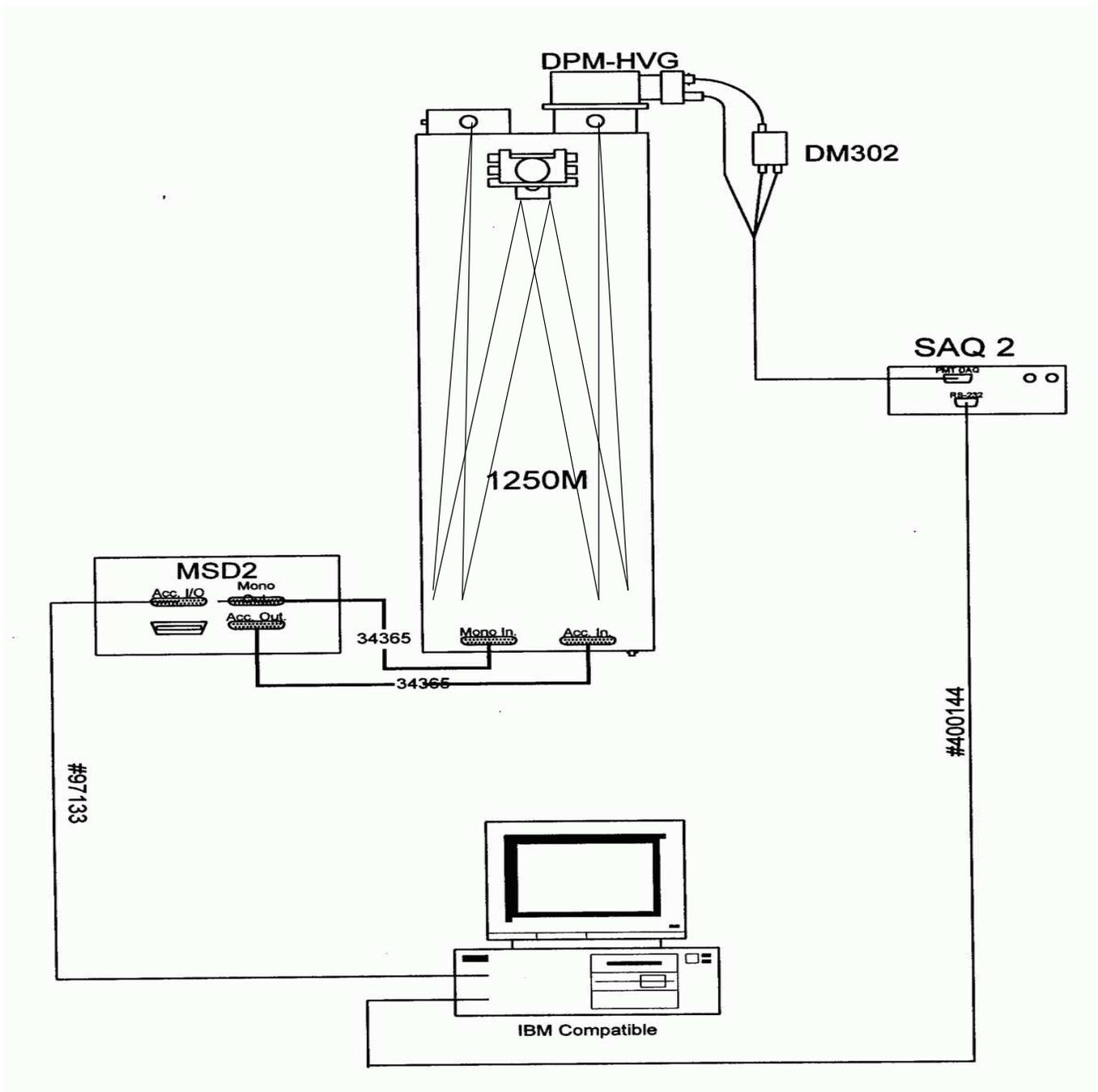


FIG. 2: Schematic of the Jobin Yvon 1250M monochromator.

measured Balmer lines, using in each case the appropriate values of n_f and n_i . From these data, 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.

4.3. 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;
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. Where the fine structure splitting in hydrogen is very small and difficult to detect (0.08 \AA in H_β), it is readily observed and measured in the alkali atoms. It decreases with n and l approximately as $1/[n^3l(1+l)]$, and so is most prominent in the P states. 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 these separations provided important clues for identifying the transitions and deducing the level structure from observed spectra. See Melissinos for an energy level digram for sodium.

Obtain various sodium spectra of varying integration times with a superposed short mercury calibration spectrum, both with and without the UV 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

$$E = E_\infty - \frac{hcR}{(m + \mu)^2} \quad (2)$$

where m is an integer, and E and μ are constants.

Determine the fine-structure splittings of the 2P levels involved in the transitions responsible for the various doublets. Check whether the doublets originating from and terminating at the same 2P level have the same separation (in wave numbers). 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. Note that in spectroscopic notation, the upper left superscript is equal to $2S+1$ and the lower right subscript is the total angular momentum

‘j’.

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.

4.4. 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 measuring 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 very 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.

5. ANALYSIS

Compute the value of m_d/m_p and an error estimate from the measured separations of the hydrogen and deuterium Balmer lines, using the mercury calibration data. Compare the results with the known ratio of the atomic weights of deuterium and hydrogen.

5.1. 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.

[1] J. Lerner and A. Thevenon, *The Optics of Spectroscopy* (Jobin-Yvon, 2000).
 [2] E. Hecht, *Optics* (Addison Wesley, 2002).
 [3] A.P.French and E. Taylor, *An Introduction to Quantum Physics* (Norton, 1978).
 [4] R. Rhodes, *The Making of the Atomic Bomb* (Simon and Schuster, 1986).
 [5] A. Melissinos, *Experiments in Modern Physics* (Academic Press, 2003), 2nd ed.

[6] S. Gasiorowicz, *Quantum Physics* (Wiley, 1996), 2nd ed.
 [7] C. White, *Introduction to Atomic Spectra* (McGraw-Hill, 1934).

APPENDIX A: GRATING PHYSICS

Figure 2 shows the optical layout in the monochromator. Note that the “source” for both this system is a narrow slit upon which an external light source is focused. 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 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, and 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 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 a diffracted image of the original slit at the focal plane of the monochromator where it then passes through an exit slit and onto the photocathode of a sensitive photomultiplier tube. The spectrum appears as monochromatic slit images spread out in the direction of dispersion of the grating. The bandpass spectrum is adjusted by rotating the grating about a vertical axis.

The gratings used in the monochromator are plane reflection gratings.

The most general form of the plane reflection grating is shown in Figure 3. Each “tread” or “riser” of the staircase reflects a narrow rectangular piece of an incident plane wave, and this piece 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 differences in path length along the reflected rays from successive grooves is an integral number of wavelengths. This condition is expressed by the grating equation

$$m\lambda = d(\sin \alpha + \sin \beta) \quad (\text{A1})$$

where α and β are the angles between the grating normal GN 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.

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

$$\frac{d\beta}{d\lambda} = \frac{1}{d\lambda/d\beta} = \frac{m}{d \cos \beta} = \frac{\sin \alpha + \sin \beta}{\lambda \cos \beta} \quad (\text{A2})$$

The figure "Reflection Grating Geometry" was removed due to copyright restrictions. Reference: Palmer, Christopher A., and E. G. Loewen. *Diffraction Grating Handbook*. Rochester, NY: Thermo RGL, 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)

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^{-1}

$$P = \frac{d \cos \beta}{m f} \quad (\text{A3})$$

where f is the effective focal length of the instrument.

In the monochromator the grating is used in a Littrow Configuration where $\alpha = \beta$, and under these conditions Equation A1 simplifies to

$$m\lambda = 2d \sin \beta \quad (\text{A4})$$

Furthermore, Equation A2 becomes

$$D = \frac{d\beta}{d\lambda} = \frac{2}{\lambda} \tan \beta \quad (\text{A5})$$

When $|\beta|$ increases from 10° to 63° in Littrow use, the angular dispersion increases by a factor of ten, regardless of the spectral order or wavelength under consideration. Once β has been determined, the choice must be made whether a fine-pitch grating (small d) should be used in a low order or a coarse-pitch grating (large d) such as an echelle grating should be used in a higher order. In this experiment, the former solution was chosen to provide a much larger free spectral range (see below).

At 4358 \AA in first order (corresponding to $\beta = 31.5^\circ$ by Equation A4), the grating in our monochromator has dispersion of 2.8×10^{-4} radians \AA^{-1} using Equation A5. With a focusing mirror of focal length 1250mm following the grating, the linear dispersion would be 0.35 mm \AA^{-1} .

The grating used in the Hydrogenic Spectroscopy experiment is ruled with $2400 \text{ lines mm}^{-1}$ ($d=4167 \text{ \AA}$). From Equation A4, light at 4358 \AA will be refracted in first order at $\beta = 31.5^\circ$ in first order and at 63.0° in 2nd order. Light emitted at this latter angle will miss the focusing mirror and thus we are dealing with essentially just 1st order diffraction.

Finally, from Equation A4 we find that the difference between two wavelengths diffracted at the same angle in

successive orders, called the free spectral range, is given by the equation

$$\lambda_1 + \Delta\lambda = \frac{m+1}{m}\lambda_1 \quad (\text{A6})$$

from which

$$F_\lambda = \Delta\lambda = \frac{\lambda_1}{m} \quad (\text{A7})$$

APPENDIX B: EQUIPMENT LIST

Item	Model
1" UV Filter	6057
1" PCX Lenses	Various
Monochromator	1250M
Photomultiplier Tube	R928
H-D Spectral Lamps	Custom
Spectral Lamps	Various
LabVIEW	