grating monochromator
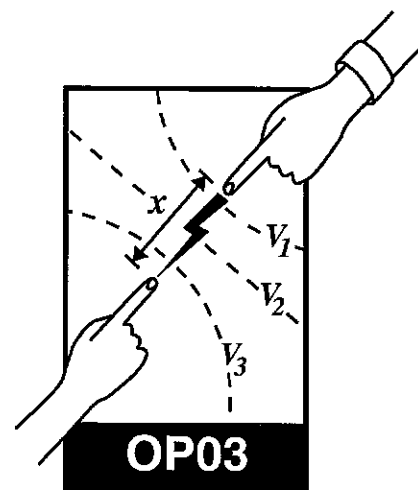
OP03

1 Introduction

The purpose of this experiment is two-fold:

(a) to give experience with experimental techniques which are widely applicable in spectroscopy;

(b) to investigate the spectrum and energy level structure of atomic hydrogen.

Your write up should include brief accounts of the various observations made and answers to the calculations and questions posed. If you do not understand any section of this manuscript please ask a demonstrator for help and advice.

Before you start the experiment a demonstrator will go through the important points and explain the optical system of the monochromator. You should then read through sections 2, 3 and 4 before beginning the setting-up procedure described in section 5.
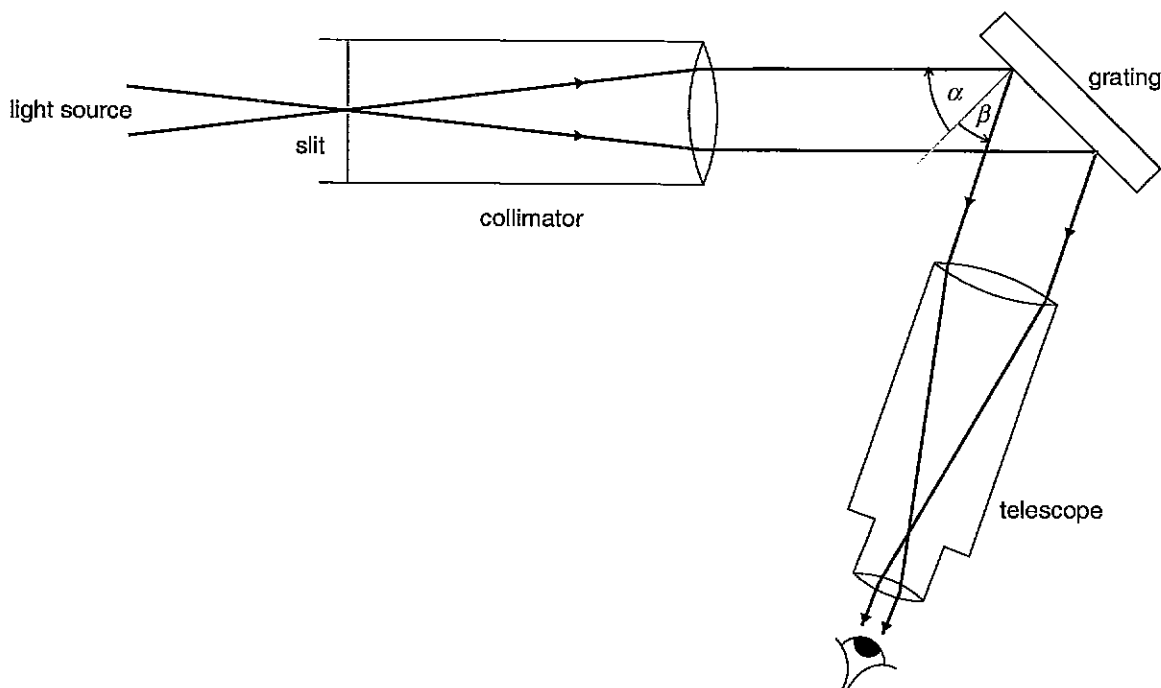
2 Spectroscopes and monochromators

Figure 1 A simple spectroscope. Note that here, as in all practical instruments, the grating consists not of slits but reflecting strips, that is, it works in reflection not transmission

When a collimated beam of light of wavelength λ is incident on a reflection grating at an angle α, constructive interference occurs in beams diffracted at the angles β which satisfy the equation

$$d(\sin\alpha \pm \sin\beta) = p\lambda \tag{1}$$

as shown in Figure 1. The order number p is usually a small integer and d is the spacing of the grating rulings; the +ve sign is used when the incident and diffracted beams are on the same side of the grating normal, and the –ve sign when they are on opposite sides of the normal. In a grating spectroscope a system of lenses, forming a collimator and telescope, is used to produce an image of a fine entrance slit. When this slit is illuminated by light containing several different wavelengths then, due to constructive interference of light diffracted by the grating, the variously coloured images of the slit are formed at different angles. When the slit is narrow these images appear as bright lines on a dark background and are known as *spectral lines*. These lines are characteristic of the chemical composition of the source.
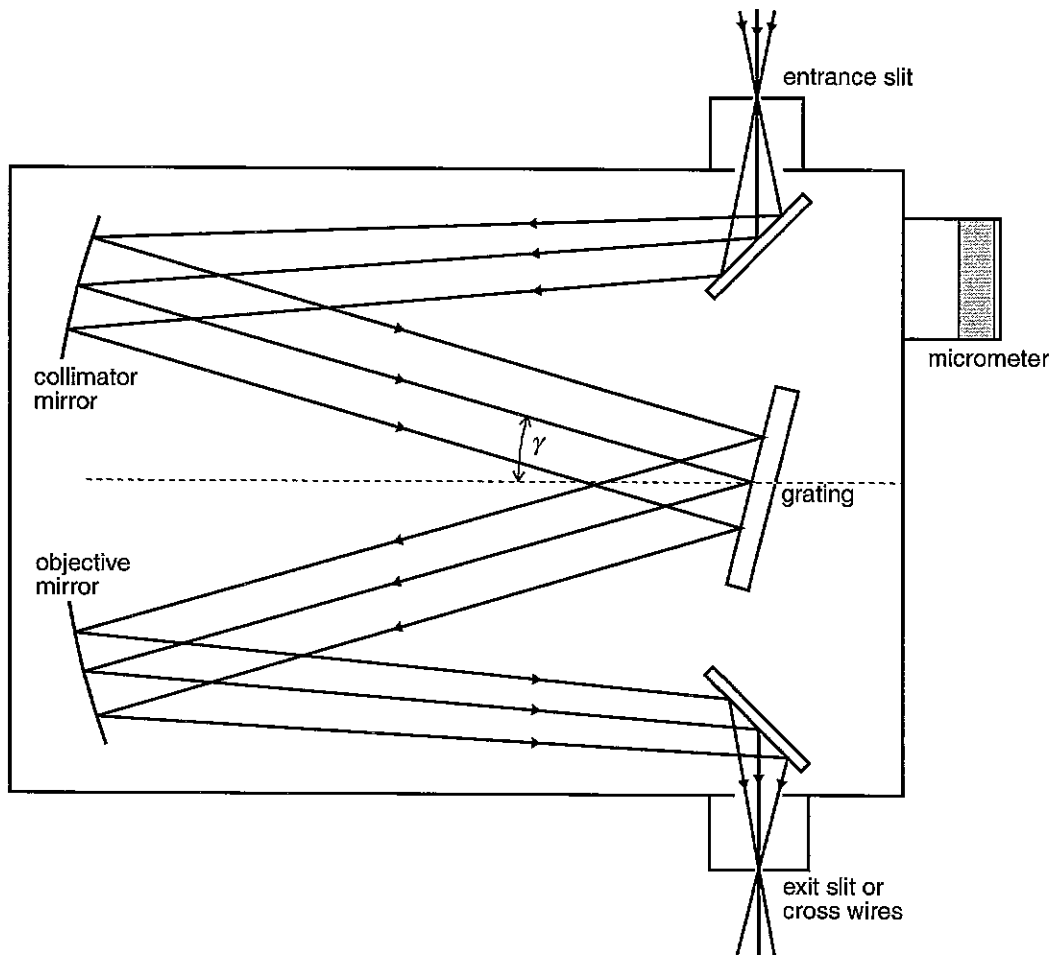

Figure 2 Czerny-Turner Monochromator

For the analysis of spectra and the determination of the spacing of atomic and molecular energy levels the highest possible accuracy in wavelength measurement is required. This is usually achieved by employing large spectrographs in which the spectra are recorded photographically. However in many experiments we want to study a line of which the wavelength is already known (for example, to see how its intensity varies with discharge conditions). Under these circumstances the wavelength measurement need only be made with sufficient accuracy to enable the line to be identified unambiguously. Thus for research purposes a less precise but more compact instrument is often more convenient. It is also desirable that the wavelength of the spectral line of interest can be determined directly from a scale or dial reading. All of these advantages are found in the *Czerny-Turner monochromator* on which this experiment is based.

3   The Czerny-Turner monochromator

In the Czerny-Turner monochromator concave mirrors are used to collimate the beam of light falling on the grating and to focus those beams diffracted from the grating, as shown in Figure 2. This means that the working range of the instrument is not restricted by the limited transmission of glass lenses in the ultra-violet region and moreover that there is no chromatic aberration. The grating is rotated by an arrangement known as a *sine-bar* which is driven by a large micrometer. The operation of the sine-bar is described more fully in section 4; it consists of a lever mechanism in which linear displacement by the micrometer is made proportional to the sine of the angle between the grating normal and the symmetry axis of the instrument. An approximate value of the wavelength of any spectral line in Ångstrom units may, in this instrument, be obtained by doubling the micrometer reading, $(1 \text{ Å} = 10^{-1} \text{ nm} = 10^{-10} \text{ m}$. You must get used to working in both Å and nm in spectroscopic work!). Other important design parameters of these instruments are given below.

Grating size	48 mm × 48 mm
Ruling frequency $(1/d)$	1200 lines per mm
Mirror diameter	63.5 mm (2.5 inches!)
Mirror radius of curvature	439 mm
Czerny-Turner angle, γ	25° 28′
Length of sine-bar, l	75.24 mm

4   Theory

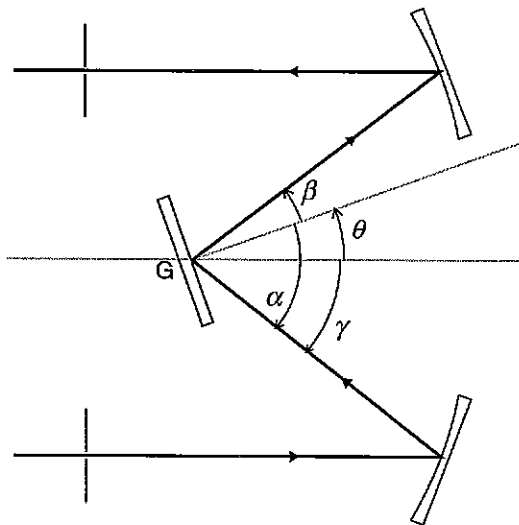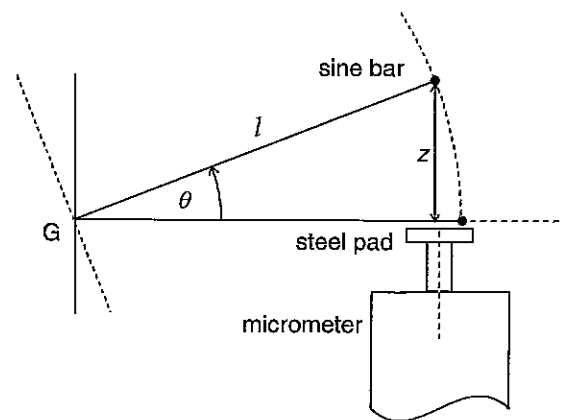**Figure 3a**   **Figure 3b**

We return to equation (1) which gives the relation between the angles of incidence and diffraction α and β respectively, the grating spacing d, and the wavelength λ and order number p.

$$d(\sin\alpha \pm \sin\beta) = p\lambda.$$

It may be rewritten in terms of the Czerny-Turner angle γ (which is constant and determined by the mirror geometry) and the variable angle θ between the grating normal and the symmetry axis of the instrument. The result is

$$\sin\theta = \frac{p\lambda}{2d\cos\gamma}.\tag{2}$$

We apply this to the present set-up in Figure 3a

The grating is rotated by a lever arm of length l which is moved by the linear displacement z of the micrometer, as shown in Figure 3b. Hence we also have

$$\sin\theta = z/l.\tag{3}$$

Combining equations (2) and (3) we have

$$\lambda = z\left(\frac{2d\cos\gamma}{pl}\right).\tag{4}$$

(a) Using the data given above, calculate the combination $\dfrac{2d\cos\gamma}{l}$

(b) How large is the grating period d compared with a typical optical wavelength?

Thus the wavelength of light transmitted through the monochromator is a linear function of the displacement z produced by the micrometer drive. This simple proportionality is very convenient for setting on a given line to moderate accuracy. However, in practice, the sine bar drive cannot be relied upon to the precision of which the instrument is capable, so in the present experiment a calibration spectrum is used (section 6).

5 Focusing and alignment procedure

5.1 Focusing of collimator

In order to illuminate the grating with a parallel beam of light it is necessary to adjust the entrance slit to be at the focus of the collimating mirror. To perform this adjustment, first rotate the grating so that the zero-order is transmitted through the instrument. Check the micrometer reading is set to zero when zero order coincides with the cross-wire of the eyepiece. Then rotate the grating to approximately 3200 on the micrometer. In this position the angle that the grating normal makes with the axis of the instrument is approximately equal to γ. Thus the zero order of the grating is reflected back towards the entrance aperture. Slacken the brass lock-screw and take out the slit. Now find the focal point of the collimating mirror by the no-parallax method (see Figure 4 opposite) using a steel needle held in a stand as the object. The side of the needle facing the monochromator should be illuminated by a small lamp. Having found the focus you need to get the slit into this position. Replace it so that it coincides approximately with this focal point and open it to its widest setting. Then carry out the no-parallax procedure on the slit using its back-reflected image. When you have done this, tighten the brass lock screw *ensuring that the slit is vertical*. Then find the position of the grating at which the back-reflected image coincides exactly with the slit. Record the micrometer reading, and using equation (3), determine the Czerny-Turner angle. Check that your result is close to the value given in section 3.
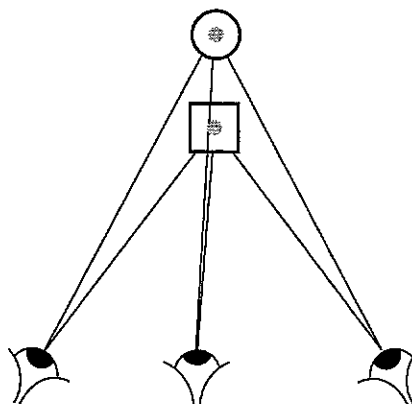
Physical situation shown from above, with three viewing angles
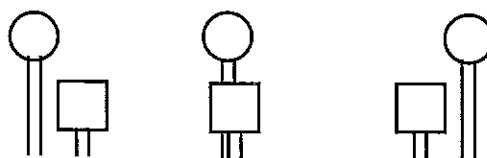
Appearance to the eye when viewed from the three directions

Figure 4 Parallax. When two visible entities are at different distances from an observer, their apparent alignment will depend on the direction from which they are viewed. This is called parallax. If there is parallax between the entrance slit and its image in the collimating mirror (back-reflected from the grating), then the focusing is incorrect and therefore the light is not properly collimated at the grating. If there is parallax between the output spectral line and the cross-hair, then the measured readings will fluctuate owing to change in the viewing angle of the observer.

5.2   Alignment of the source

The next task is to illuminate the instrument properly using a mercury lamp and condensing lens. Two conditions need to be fulfilled:

(a)   The lamp and lens must be on the optic axis of the collimating system.

(b)   There must be a sharp image of the lamp on the slit.

There is in most spectroscopic work a third condition, which is to fill the grating with light by making sure the angle the lens subtends at the slit is large enough. This makes full use of the resolving power of the grating and the light-gathering ability of the instrument. However, if this is done in the present experiment aberrations become a problem, and it is best instead to form an image of the source on the slit with approximately unit magnification. The grating is then not completely filled with light, but this is not serious provided that we satisfy conditions (a) and (b). Proceed as follows. Adjust the height of the lens by putting it close to the slit. Switch the mercury lamp on and form an image of it on the slit with approximately unit magnification (that is, the distance of the lamp from the lens is roughly equal to that from the lens to the slit). To do this, you will need to adjust the height of the lamp; a demonstrator will show you how to do this safely.

Condition (a) is not yet satisfied; to do this, first rotate the grating so that the monochromator is set to transmit the strong green line 546 nm. Then remove the lens from the system. Put your eye close to the instrument and look into the spectrometer (not at the image). Then adjust the lateral position of the source until light entering the spectrometer falls centrally on the grating. Finally, replace the condensing lens between the source and entrance slit and bring an image of the source to a sharp focus

on the slit. Put your eye close to the instrument again and look into it as before. There should be a uniform elliptical patch of light falling centrally on the grating.

5.3 Focusing of objective mirror

The position of the cross-hair in the exit aperture should now be adjusted. Orient it × rather than +; this makes it easier to set it on a spectral line. We require the cross-hair to be placed precisely where the spectral line comes to a sharp focus. First move the cross-hair in and out by large amounts (centimetres) while observing the rectangular patch of light falling on it from the monochromator, in order to get a rough sense of where the focal position is (*i.e.* where the line is sharpest). Place it at your best estimate of the correct position, then view the cross-hair through the high power eyepiece and perform a fine adjustment using the no parallax method (i.e. no parallax between the cross and the spectral line). N.B. you are still adjusting the cross-hair, not the eyepiece! The no parallax method is precise but can be difficult to apply owing to distortion of the image as you move your eye around to view from different directions. It is sufficient to use modest changes in viewing angle, so as to avoid this distortion.

The width of the entrance slit should now be adjusted to the optimum value. If the slit is too wide, the accuracy of the wavelength measurements will be poor. If it is too narrow, you will have difficulty in observing the weaker hydrogen lines. Bring the pair of yellow lines at 577 nm and 579 nm into view and check that you can resolve them easily, then observe a few of the weaker lines of mercury to make sure they are visible.

The apparatus should now be in good adjustment for quantitative experiments. Ask a demonstrator to check it before you proceed with the calibration in section 6.

6   The visible spectrum of hydrogen
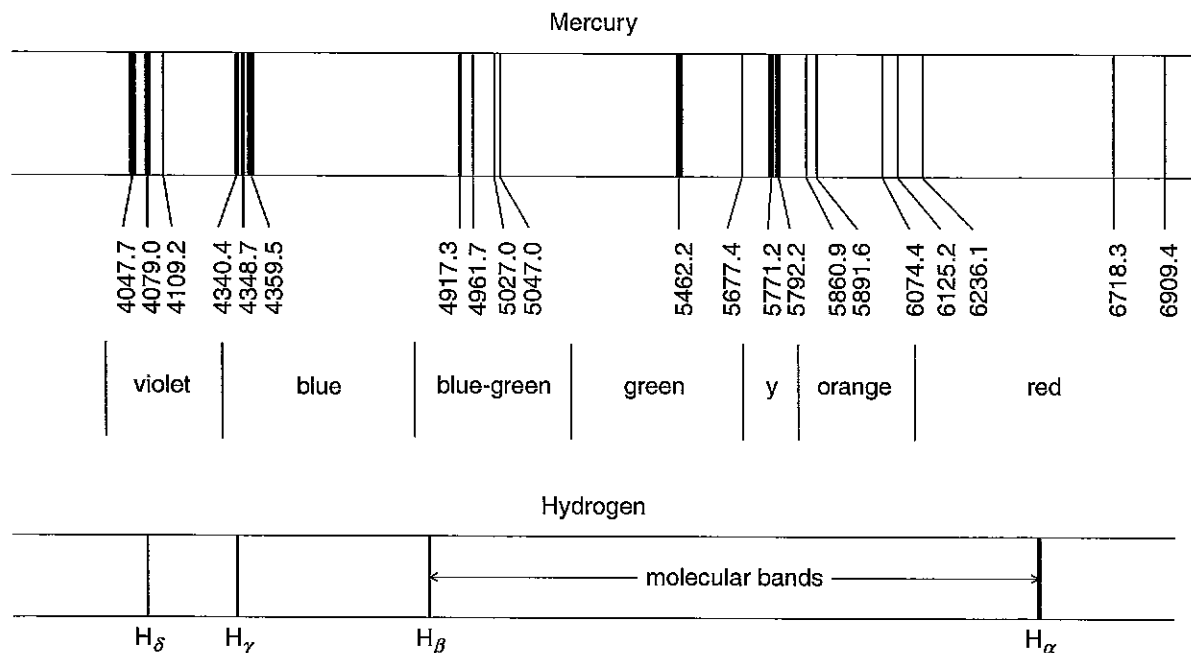
Figure 5 Schematic of mercury and hydrogen spectra. The wavelengths given are vacuum wavelengths (in Å) because they are required in this particular experiment. Note, though, that you will generally find air wavelengths quoted for visible lines as these are more usually needed in practice. For example, the well-known strong mercury green line normally referred to by its air wavelength as "the 5461 line" appears in the diagram above as 5462.2 Å. [The refractive index of air is about 1.0003.]

The instrument is to be calibrated using the known wavelengths of the mercury lines shown in Figure 5. If this calibration is performed carefully, a precision in the value of R_H of better than 0.01% can be achieved. Note, however, that a significant systematic error may arise if the width, and hence possibly the centre position, of the slit is changed between the calibration procedure and the measurements on the hydrogen spectrum.

Before proceeding, make sure you understand the logic of what you are about to do. Ultimately we would like to use the monochromator to measure some unknown wavelength λ (*e.g.* a line in the hydrogen spectrum). What one actually records using the instrument is the micrometer reading z. Therefore we need to know the relationship between λ and z. The basic theory gave us such a relationship (equation (4)), but that theory treated an ideal instrument, with no mechanical imperfection, *etc.*, so equation (4) is obeyed only approximately in practice. We can get a much more precise equation relating z and λ by using a calibration spectrum, in this case the spectrum of mercury. By finding the value of z (micrometer reading) for a set of known λ, we can plot on a graph the accurate relation between z and λ, and then use it for interpreting further measurements of unknown wavelengths.

Of course for this we rely on someone else's work who measured the mercury spectrum, and they must have used a different method to calibrate their instrument. Such a reliance is involved in most precise scientific work.

With the mercury lamp in position, record the micrometer readings for all the visible lines. Several readings should be made for each line, but the lines must always be approached from the same side to avoid any back-lash errors. Figure 5 sets out the approximate positions and intensities of the lines, so that you should be able to identify them unambiguously. For example, the gap between the red and orange lines is similar to the gap between orange and green: this gives you an idea of how far you should expect to go past orange before seeing the final red ones.

Enter your data into a scientific data plotting computer program (you may need guidance from a demonstrator, or consult appendix A), and obtain the plot of micrometer reading as a function of true wavelength. N.B. the known wavelength should be on the horizontal axis, the measured micrometer reading on the vertical axis.

Now consider how this information can best be used. The following procedure will give you some training in the handling of this type of data using fitted curves. Note that this experiment is capable of yielding results that are accurate to about 0.02%. You should ensure that your calculations and the quantities obtained from the plots have enough significant figures to achieve this.

Clearly the data lie close to a straight line, as expected. Therefore first instruct the computer to furnish the parameters of the best straight line fit. Next, obtain the "residuals", that is, the differences $z_{data} - z_{fit}$, and plot them (versus known wavelength). The residuals plot gives information on the degree to which the fitted straight line has correctly captured the main trends in the data. You should see on this plot the random fluctuations present in the data, but may also see strong evidence that the straight line fit is not adequate to capture what the data are really showing. Therefore, next instruct the computer to obtain the parameters of a quadratic fit (*i.e.* polynomial function of degree 2), and plot the new set of residuals. The quadratic function makes a good job of providing the desired calibration curve, so this is what you should use when interpreting the hydrogen measurements. Also extract the standard deviation σ_{res} of the set of residuals. As a check, make sure it agrees with your own rough estimate of the standard deviation which you can obtain simply by looking at the residuals plot and estimating by eye.

Label and print out all four graphs for your report.

σ_{res} gives a measure of how far the calibration curve might be shifted up or down and still provide a reasonable fit to the data. You should use this as the experimental uncertainty associated with each use of the calibration curve. Appendix 2 gives a detailed discussion of this point for the keen student.

The fitting procedure results in a formula for z in terms of lambda:

$$z = a\lambda^2 + b\lambda + c \pm \sigma_{res}.$$

It came out this way because the wavelength was the known quantity, while the micrometer reading was the (noisy) observed quantity. Obviously, when you use this as a calibration curve for measuring unknown wavelengths, you need to invert the formula, so as to obtain an expression for the wavelength as a function of z. Fortunately a quadratic equation is easy to invert. To relate uncertainties in z to uncertainties in λ, observe that

$$\frac{dz}{d\lambda} = 2a\lambda + b.$$

Remove the mercury lamp and insert the capillary discharge tube. Without moving the cross-hair, look at the patch of light on the grating, as before (use the red line) and put the lamp in such a position that the illumination is correct (check with a demonstrator). Do not move the lens; this should remain where it was for the calibration procedure. Note that excited hydrogen atoms are only one of the many species produced in the discharge. In particular, strong emission bands of H_2 and OH^- molecules may be seen in the region between the H_α and H_β lines. In identifying the lines, you can be guided by the approximate relationship quoted in section 3. If you are unsure of the identification of the lines, check with a demonstrator (see Figure 5 for guidance).

Measure the wavelengths of the four visible lines of atomic hydrogen taking care to distinguish the sharp atomic lines from the band-heads of the molecular spectra. If you find it hard to see H_δ, try turning off extraneous light sources and shielding your eyes so that they become dark-adapted (wide pupil diameter). It may be necessary to widen the slit somewhat for this particular measurement, but avoid resorting to that until you have completed all other measurements.

Use the calibration curve to obtain the correct vacuum wavelengths of these lines. The wavelengths of the calibration lines in Figure 5 are vacuum values so your results need no correction, even though the experiment itself is carried out in air.

The wavelengths in vacuo of the Balmer lines of atomic hydrogen are found to satisfy the expression

$$1/\lambda_n = \tilde{\nu}_n = R_H\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \quad \text{where } n = 3, 4, 5, ...\infty. \tag{5}$$

Calculate the separate values of R_H together with their uncertainties from your data. The errors on each value of R_H may be determined by combining the errors due to the calibration and to the uncertainty in measurement of the hydrogen lines. Finally, the separate values of R_H may be combined to give the weighted mean $\bar{R}_H$ and the standard error of the mean $\delta\bar{R}_H$, and your result should be expressed as $\bar{R}_H \pm \delta\bar{R}_H$ in either cm^{-1} or m^{-1}. Compare your result with the theoretical value (see section 7).

7   Bohr theory for atomic hydrogen

It is simplest first, as Bohr did, to take the nucleus as fixed at the origin. This corresponds to assuming that the proton is infinitely massive compared with the electron. Bohr postulated that the angular momentum of an electron orbiting the nucleus of a hydrogenic atom is given by

$$m_e vr = n\hbar \quad \text{where } n \text{ is an integer.} \tag{6}$$

The centripetal acceleration is determined by the Coulomb attraction of the nucleus:

$$\frac{m_e v^2}{r} = \frac{Ze^2}{4\pi\varepsilon_0 r^2}. \tag{7}$$

Substituting from equation (6) gives

$$\frac{1}{r} = \frac{Ze^2 m_e}{4\pi\varepsilon_0 n^2 \hbar^2} .$$ (8)

The total energy of the system is the sum of the kinetic and potential energies:

$$E_n = \frac{1}{2} m_e v^2 - \frac{Ze^2}{4\pi\varepsilon_0 r} .$$

Substituting from equations (7) and (8) gives

$$E_n = -\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2 \frac{m_e}{2\hbar^2} \frac{1}{n^2} .$$ (9)

The energy of a photon emitted in a transition from a level with quantum number n to one with quantum number n' is given by

$$h\nu_{nn'} = hc\,\tilde{\nu}_{nn'} = E_n - E_{n'} = -\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2 \frac{m_e}{2\hbar^2}\left(\frac{1}{n^2} - \frac{1}{n'^2}\right) .$$ (10)

The Rydberg constant for atomic hydrogen, $Z = 1$, is therefore given in the approximation of an infinitely massive nucleus by

$$R_\infty = \left(\frac{1}{4\pi\varepsilon_0}\right)^2 \frac{m_e e^4}{4\pi c \hbar^3} .$$ (11)

A calculation in which the nucleus has mass M also gives equation (11) except that the electron mass, m_e, is replaced by its reduced mass

$$\mu = \frac{m_e M}{m_e + M} .$$ (12)

An interesting consequence of this analysis is that the Rydberg constant for deuterium differs slightly from that of hydrogen and gives rise to an isotope shift between the spectral lines of light and heavy hydrogen.

For the particular case of hydrogen, we have,

$$R_H = \left(\frac{1}{4\pi\varepsilon_0}\right)^2 \frac{e^4}{4\pi c \hbar^3} \times \frac{m_e m_p}{m_e + m_p} .$$ (13)

where m_p is the proton mass.

Evaluate R_H to sufficient accuracy to allow critical comparison with your experimental result using the following data:

$$\varepsilon_0 = 8.8542 \times 10^{-12}\,\text{Fm}^{-1}$$
$$e = 1.6022 \times 10^{-19}\,\text{C}$$
$$c = 2.9979 \times 10^8\,\text{ms}^{-1}$$
$$\hbar = 1.0546 \times 10^{-34}\,\text{Js}^{-1}$$
$$m_e = 9.1095 \times 10^{-31}\,\text{kg}$$
$$m_p = 1.6726 \times 10^{-27}\,\text{kg}$$

Notice that the reduced mass μ represents approximately a part per thousand correction, compared to m_e. Comment on whether your experimental result gives clear evidence that R_H and not R_∞ is observed.

Appendix 1   Computer software for data plotting

A1.1   High-level programming

A high-level programming package such as Matlab or its shareware cousin GNU Octave is excellent for all sorts of scientific data manipulation and plotting. For this approach, first enter your data into a text file, for example in two columns separated by spaces, and then at the Matlab or Octave prompt, use commands such as

```
d = load('mydata.txt')
x=d(:,1); y=d(:,2);
plot(x,y,'+')
```

If there are several y readings at each x, then you can use for example

```
y=d(:,2:n);
```

where n is the number of readings and I assumed your text file contains the data arranged in columns. To get the mean and standard deviation of each set, keep in mind that standard functions such as mean and std act on each column of a matrix, so first transpose:

```
y = y';
x = x';
```

and then you can use for example

```
yav = mean(y);
ystd = std(y);
```

If for each data point you performed n independent readings of the same thing, then the statistical uncertainty of the average is given by the standard deviation of the set of observations, divided by $\sqrt{(n-1)}$, so you can use

```
yerr = ystd / sqrt(n-1);
```

to obtain an estimate of the experimental uncertainty of each value in yav. Note, however, that if all the readings in a set agree, then this gives zero, an unacceptable underestimate. In such a case it should be replaced by your best estimate of how uncertain you think your observations really were.

To learn how to fit polynomial curves to the data, type

```
help polyfit
```

Once you have the coefficients cf of a fitted curve, you can plot both the smooth curve and your data points on the same graph, for example using

```
xcurve = linspace( min(x), max(x), 1000 );
ycurve = cf(1) * xcurve .^2 + cf(2) * xcurve + cf(3);
plot(x,y,'+', xcurve, ycurve)
```

where I showed for illustration the case of a quadratic fit. Note that when taking the square of the set of xcurve values, you need the dot in front of the $\wedge$ operator. This is a short-hand to avoid the need to write a "for loop", it means the operation is to be performed on each element of the array xcurve. Regard ".$\wedge$" as a single operator (*i.e.* no space between the dot and the $\wedge$).

It should now be obvious how to get the residuals. First obtain y_{fit} values just at your data points:

```
yfit = cf(1) * x.^2  + cf(2) * x + cf(3);
```

and then

```
yresid = y - yfit;
figure(2)
plot(x,yresid,'.')
```

Obtain the standard deviation of the residuals by

```
sigmares = std( yresid );
```

A good way to present data is to put the data, fit and residuals on a pair of graphs one above the other, as follows:

```
subplot(2,1,1)
plot(x,y,'+', xcurve, ycurve)
subplot(2,1,2)
plot(x,yresid,'.')
```

Use the Matlab commands title, xlabel and ylabel to add labels to your graph. You can put the cf values into a legend using

```
text(xlocation, ylocation, string)
```

where you supply the x- and y location on the graph, and for the string you could use something like

```
string = ['Quadratic fit: a,b,c=' num2str(cf)]
```

(square brackets are used in Matlab and Octave to concatenate arrays or strings). If there is not enough room for this legend, then adjust the axis limits using the axis command. The syntax is

```
axis( [xmin xmax ymin ymax] )
```

Note the use of square brackets for the list, and round brackets for the function.

A good title for the residuals plot would be

```
title( ['Residuals: \sigma=' num2str( sigmares ) ] )
```

A1.2   Plotting package

Software devoted to plotting, such as Origin, usually has a mouse-driven front end and this can make it easier to get started. However, it can be difficult to figure out how to do scientific tasks such as curve fitting, and it takes longer to create multiple figures starting from similar data, because you have to re-enter labels *etc.* by hand. Also, you should adjust the plotted points so that they are neither too large nor too small, and you should normally use crosses (+) or error-bar symbols, not some other shape.

For a linear fit, in the program Origin, first select the x and y data columns, then go to the Tools menu and select linear fit.

To get a residuals plot in Origin, you will need to create a new column in the spread sheet using the column menu, and then right-click the new column, and select Set column values. In the box that appears, type in the appropriate formula, such as col(C) = col(B) - (a + b*col(A)) where for a and b you should substitute the parameter values obtained from your straight line fit, and I assumed the x (wavelength) values are in col(A), while the y (micrometer) values are in col(B). You can now plot col(C) versus col(A).)

To get the parameters of a quadratic fit, use the analysis menu.

Appendix 2   Interpreting a fitted curve

Fitting a curve to data is an extremely important scientific tool. It is mostly used to extract the values of various parameters, such as the location, height and width of a peak in the data. Various types of question arise: is the fit a "good" fit? how well are the parameters of the fit determined by the data? what uncertainty is associated with the use of such a curve for calibration of an instrument? Here we will focus on the last question.

Suppose for the sake of argument that we are fitting a quadratic curve to a set of data, as in the monochromator experiment, and we wish to use this curve as a calibration curve. We would like to know to what degree of accuracy we can trust this calibration.

There are two issues: first, is the instrument well modelled by a quadratic function? second, supposing that it is, how precisely have we been able to obtain the true curve? The first question is about systematic uncertainty, the second is about statistical uncertainty.

Consider first the idealised case of no systematic error. Each time we observe a known wavelength, we add one more point to our data. This builds up the number of values in our set of residuals. The standard deviation of the set will not change much as we go from, say, 10 to 20 to 30 observed wavelengths, but we should expect that this increased information should be making the calibration more reliable. It is. As long as we are sure the instrument is very well modelled by a quadratic function, then the uncertainty (1 standard deviation) to be associated with any single use of the calibration curve would be given by

$$\sigma_{cal} \text{ (statistical)} = \frac{\sigma_{res}}{\sqrt{n-3}}$$

where n is the number of data points. This is substantially smaller than σ_{res}!

However, we can't rule out the possibility that small deformities in the mechanical mechanism, such as an indentation on the pad on which the micrometer bears, would lead to a systematic departure from a quadratic function (the sine-bar length is about 75 mm, therefore it only requires an indentation of depth 10 μm to introduce a part per 10000 shift in the grating angle). This means that, no matter how many observations we make, the calibration curve will always be wrong, simply because it is the wrong function to describe the instrument. The statistical error gets smaller as more observations are made, but the systematic error does not.

How large is the systematic error, then? This is always hard to assess, and each experimental apparatus needs to be considered individually. However, it is obvious that if the true calibration curve departed strongly from the one you picked, then you would notice because the residuals would not look randomly distributed. Therefore we can argue that the systematic error is no larger than σ_{res}, but without further investigation we can't claim that it is smaller than σ_{res}.

The conclusion is that the uncertainty to be associated with any single use of the calibration curve is σ_{res} if you do no further analysis at this stage (and that is acceptable). If you want to take things further (optional), then carry out a search for systematic effects. For example, you could group the data points. For each group, find the mean $\bar{y}$ and the statistical error on the mean $\sigma_{\bar{y}}$. Then fit a curve to these $\bar{y}$ and examine whether the scatter in the residuals is consistent with the error bars $\sigma_{\bar{y}}$.