

Atomic Spectroscopy

Before starting this experiment please read the important safety information associated with it provided on ELE.

Quantum mechanics predicts that electrons bound to the nuclei of atoms occupy discrete energy levels, which can in principle be determined by solving the Schrödinger equation subject to appropriate boundary conditions. When the electrons are excited, they return to the equilibrium by making transitions from the excited state back to the lowest energy state available, and the energy released in doing so can be in the form of photons. These photons have energies characteristic of the species of atom involved and so different atoms have different atomic spectra.

The purpose of this experiment is to investigate the atomic spectrum of hydrogen, using the known lines of neon as a calibration.

The experiment can be extended to an investigation of the more complicated spectrum of helium and to the use of a USB fibre spectrometer for data acquisition.

Theory

Hydrogen

In practice the Schrödinger equation is only exactly soluble for the simplest atom: hydrogen (and even then there are some complications that give rise to fine structure in its atomic spectrum). A simplified diagram showing the energy levels for the electron in a hydrogen atom is shown in figure 1. The vertical lines show some of the transitions that can occur as an excited electron returns to the ground state.

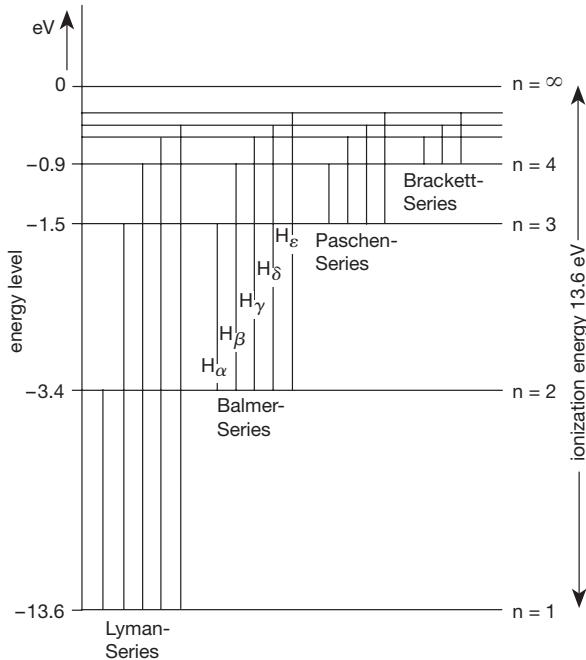


Figure 1: Simplified energy level diagram for the electron bound to a hydrogen nucleus. n is the principal quantum number, and $n = \infty$ corresponds to ionization.

These transitions are grouped as follows:

The Lyman Series includes all transitions in which the final state is the ground state (principal quantum number $n = 1$). The photons involved in these transitions are in the ultraviolet region.

The Balmer Series includes all transitions in which the final state has $n = 2$. The photons involved in the lowest three or four transitions of the Balmer series are in the visible region, and these are the transitions that we will be investigating.

Two further series are shown, both of which involve infrared photons.

The energy levels for the hydrogen atom, calculated either by using the Bohr model, or by solution of the Schrödinger equation, are given by:

$$E_n = -\frac{Ry}{n^2}, \quad (1)$$

where the Rydberg constant $Ry = m_0 e^4 / \left(2 (4\pi\epsilon_0)^2 \hbar^2 \right)$ has the value 13.6 eV.

For the Balmer Series the photon energies are therefore given by

$$E_n = Ry \left(\frac{1}{2^2} - \frac{1}{n^2} \right), \quad (2)$$

where n is one of the integers 3, 4, 5 etc.

Calculate the energies and wavelengths of the first few photons in the Balmer series and verify that they are in the visible region. As n increases the energies of successive members of the series get closer together, converging to a limit. What is the limiting energy and wavelength of the series.

Solution of the Schrödinger equation for the hydrogen actually involves two further quantum numbers, ℓ and m , both associated with the conservation of angular momentum that one expects in a spherically symmetric system. To a first approximation neither of these quantum numbers affects the energy levels of the hydrogen atom, but the quantum number ℓ becomes important in helium and is therefore worth mentioning now. ℓ is an integer which is constrained to be less than n . Figure 2 shows the energy levels of hydrogen separated into the different allowed values of ℓ .

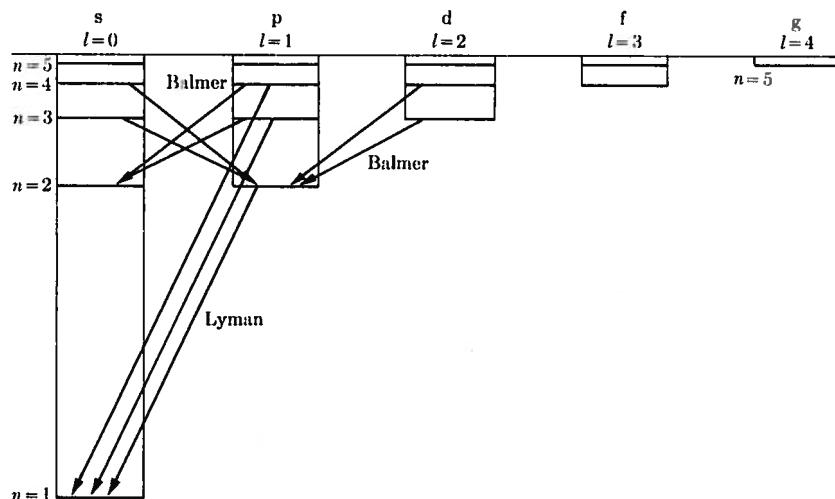


Figure 2: Hydrogen energy levels separated into different values of ℓ . The allowed optical transitions have to change ℓ by ± 1 .

Also shown are the allowed optical transitions which have to satisfy the “selection rule” $\Delta\ell = \pm 1$ because of angular momentum conservation (details are beyond the scope of this manuscript). Note that there are three distinct transitions contributing to each spectral line of the Balmer series. For instance, the three transitions $[(n = 3, \ell = 0) \rightarrow (n = 2, \ell = 1)]$, $[(n = 3, \ell = 1) \rightarrow (n = 2, \ell = 0)]$ and $[(n = 3, \ell = 2) \rightarrow (n = 2, \ell = 1)]$ all produce photons of the same energy. We will see in a moment (in the extended experiment) that this is not the case for helium. The figure also introduces some spectroscopic notation that we will use later (and which you will find in text books): levels with $\ell = 0$ are called “s” levels; those with $\ell = 1$ are p levels; $\ell = 2$, d levels; $\ell = 3$, f levels and then the labelling proceeds

alphabetically. Thus the ground state is the 1s state (the principal quantum number being 1). The first excited level consists of two states, the 2s and the 2p states, and so on.

Neon

The neon lamp is provided to calibrate the diffraction grating, and to confirm the calibration of the spectrometer. You should use the following values for this purpose:

Line colour	Wavelength (nm)
yellow	585
green	540

Helium (extended experiment only)

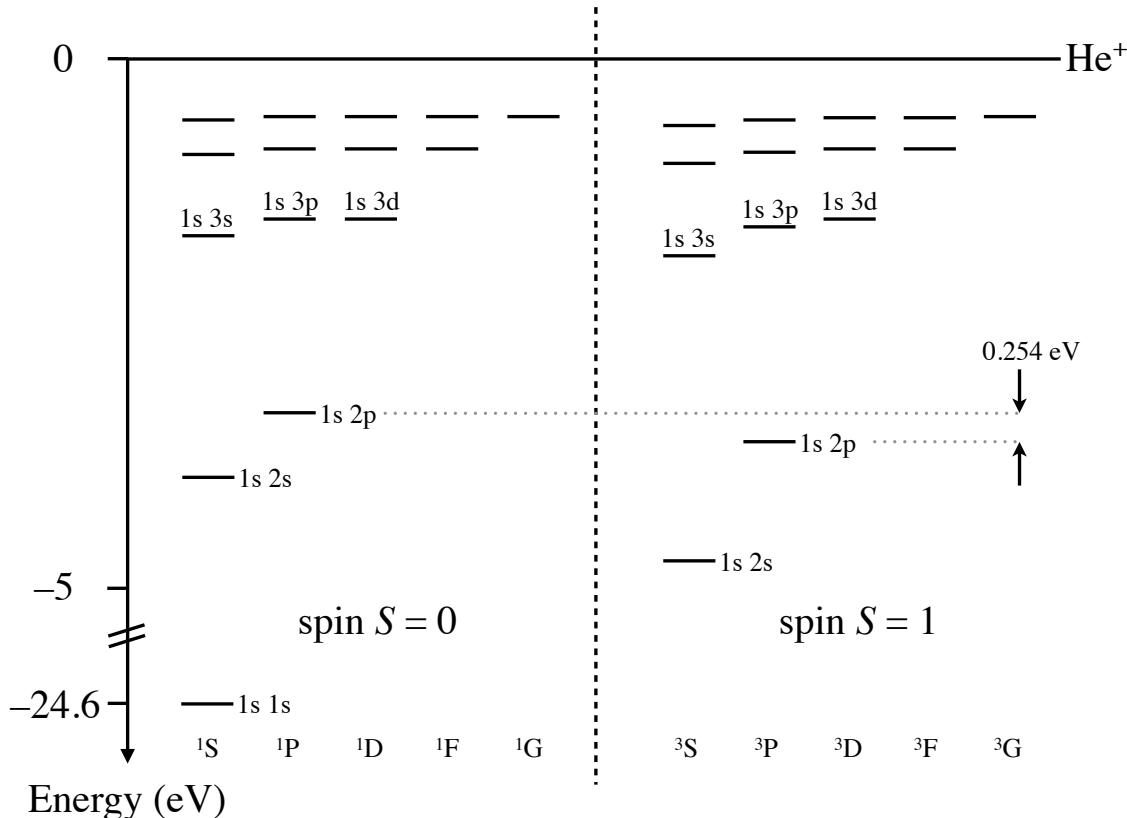


Figure 3: Energy levels of the helium atom, in which one electron remains in the ground state while the other is excited.

We can immediately see that helium is going to be more complicated if we consider the ionization of helium. Helium has two electrons. The first electron is relatively easy to ionize because the other electron partially screens it from the charge of the nucleus. Therefore,

instead of feeling the full nuclear charge $Z = +2 e$ it feels a somewhat reduced charge (actually about $Z_{\text{eff}} = 1.34 e$). The ionization energy is given by

$$E_{\infty} = RyZ_{\text{eff}}^2 \quad (3)$$

Thus the ionization of the first electron requires an energy of 24.6 eV, while the ionization energy of the second electron is 54.4 eV. The screening effect of the electrons is further complicated by the fact that different values of ℓ result in different amounts of screening. Fortunately, the excited states that we are interested in all have one electron remaining in the ground (1s) state and the other electron being excited to states with $n > 1$. This means that the orbital radius of the excited electron is large compared to that of the other electron, so the excited electron always experiences an effective nuclear charge of $+1 e$. This enables a direct comparison between its energies and those of the electron in hydrogen.

One complication that we cannot escape is spin. Each electron possesses a spin of $\pm 1/2$, and quantum mechanics dictates that the spins of the two electrons either align to give a total spin $S = 1$, or anti-align to give a total spin of $S = 0$. Whether the spins align or anti-align has a profound effect on the spatial wavefunction of the two electrons, because of the Pauli Exclusion Principle. You are encouraged to read up on the details of this, but the upshot of it is that all the states with $S = 1$ have lower energies than the equivalent states with $S = 0$. The resulting energy-level diagram for helium is shown in figure 3. The diagram is split into two sections: states with $S = 0$ on the left and those with $S = 1$ on the right. Note that every state on the left has its equivalent state on the right, except the ground state – in this state, both electrons occupy the same spatial state (the 1s state) and therefore must have anti-parallel spins. Some of the states have been labelled to indicate the quantum numbers of the individual electrons. You will notice that the first electron is always in the 1s state. Therefore the zero of energy corresponds to singly ionized helium. Also note that the difference in energy between equivalent states with $S = 0$ and 1 becomes less pronounced for larger values of the quantum numbers n and ℓ . This becomes important later.

In our experiment we are limited to observing transitions in the visible part of the spectrum and therefore all the transitions we will observe will be to the final states 1s 2s and 1s 2p with $S = 0$ and 1s 2p with $S = 1$, which can be thought of as equivalent to the Balmer series in that the final states for the excited electron all have $n = 2$.

Safety

The gas discharge tubes require a voltage between 1 kV and 5 kV to operate. The power supply provided delivers this voltage, but is current-limited to 2.5 mA, which is well below the safe limit. It is nevertheless sensible to avoid touching exposed metal when the power supply is switched on. Do not use any power supply other than the one provided.

The discharge tubes are fragile and made of glass. Please ask your demonstrator, or the laboratory technician, to connect and disconnect the tubes when required. *Do not remove the tubes yourself.*

Note to demonstrators: there are two designs of discharge tubes in the lab, one having narrow tips at each end and one having wider ones. The plastic adapters attached to the right-angle contact bars allow attachment of both types: for the wider tip design, the knurled caps should be screwed into the adapter; for the narrow tip design the caps should be removed.

Experiment

Low-pressure gas within a gas discharge tube is subjected to a large electric field. The gas ionizes releasing electrons. Collisions leave the gas atoms in various states of excitation, and characteristic spectral lines are produced as the excited atoms return to their ground states. To operate these lamps, ask a demonstrator or the Laboratory technician to install the lamp in its holder, then gradually increase the voltage applied until the lamp starts to glow. Once the lamp is glowing, it is normal for the voltage to drop even if you continue to turn up the voltage dial.

Two methods are used to measure the wavelength of the emitted light. The first method, which is more visual, involves observing the lines through a diffraction grating. The second method (for the extended experiment only), which is more accurate and more sensitive, uses a optical fibre spectrometer.

Method 1

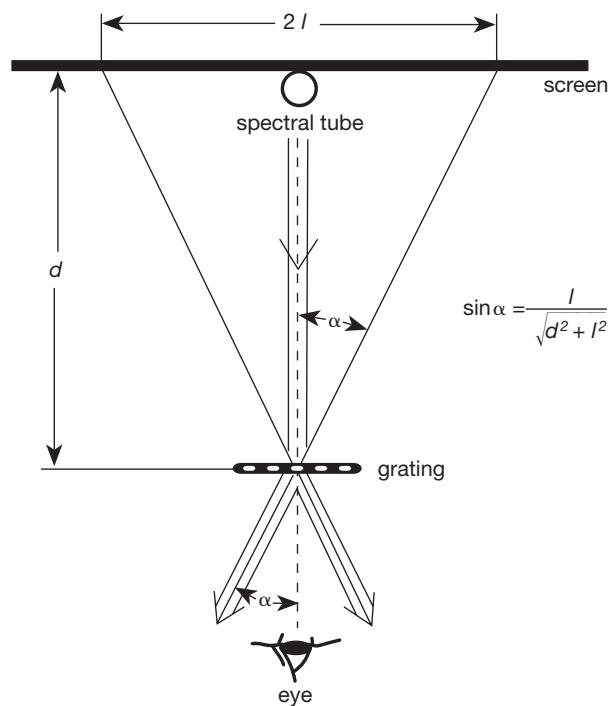
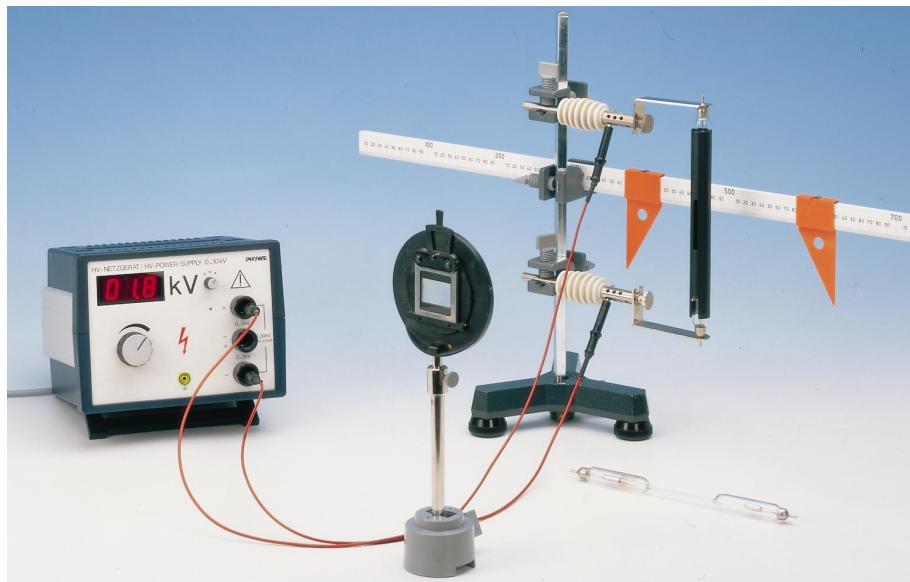


Figure 4: Top: picture of the experimental apparatus. Bottom: a diagram of the experiment showing the measurements that have to be made. Note, the orange pointers are optional. Note that the symbols in the formula for $\sin \alpha$ are the dimensions d and l also shown in the diagram.

A typical experimental arrangement and a diagram of the geometry of the experiment are shown in figure 4. When setting up the apparatus, note that maximising the distance d will improve accuracy.

The grating disperses the light into its component wavelengths, and the wavelengths can be calculated using the grating equation:

$$p\lambda = d_g \sin \alpha, \quad (4)$$

where d_g is the grating constant (the distance between adjacent lines of the grating), and p is the order of diffraction (an integer greater than or equal to 1). The grating provided nominally has 600 lines per mm, but you should use the known wavelengths of emission lines of neon to determine d_g directly.

Measure as many lines for hydrogen as you are able to see – there should be three. Use equation (2) and plot an appropriate graph to obtain the Rydberg constant.

If you are doing the extended experiment, measure as many lines as you are able to see for helium. Analysis of the helium lines is discussed in the next method.

Method 2 (extended experiment only)

In this method, the diffraction grating and the observer's eye are replaced by a USB-driven optical fibre spectrometer. Light enters the spectrometer through an optical fibre and to acquire a spectrum all one has to do is to point the end of the optical fibre at the lamp, and control the spectrometer using the software program Overture.

Clamp the post holding the optical fibre to a retort stand so that the fibre is a few millimetres from the lamp and is pointing towards it. Look at the resulting spectrum using Overture, and make fine adjustments to the fibre position to maximise the intensity of the peaks in the spectrum. Choose an exposure time that maximises the peaks without saturating them. Take spectra in this way for each of the three lamps, exporting the data to a spreadsheet program for further analysis.

Repeat the analysis of the hydrogen lines described above.

Check that the neon lines have the wavelengths given in the table above. Check out the full list of neon wavelengths on http://physics.nist.gov/PhysRefData/ASD/lines_form.html (search for "Hg i" to find the lines for singly ionized neon), and identify any other lines found in the range 400 to 600 nm. Note that there are a very large number of lines – the ones you should consider are those with the highest intensities in the table. Do you notice anything odd about the yellow neon line?

For helium some of the lines observed are part of two Balmer-like series, one with $S = 0$ and one with $S = 1$. From the discussion above, one would expect the differences in energy between these two sets of lines to be dominated by the difference in energy between the $1s$ $1p$ levels having different spins which is marked in figure 3 (the upper levels have smaller splittings especially those with larger values of ℓ). Make a list of the wavelengths observed between 400 and 730 nm and convert each of these to energy. Look for pairs of lines having the same difference in energy. These are the members of the two Balmer-like series. Once you have identified these (not before!) you can confirm your identifications by looking at http://physics.nist.gov/PhysRefData/ASD/lines_form.html.

Possible further extensions

Find as many light sources as you can, accessible from the laboratory, measure their spectra and explain what you observe in as much detail as possible.