

Laboratory – Atomic Spectroscopy

Warning: This experiment uses spectral lamps that can be both bright and emit ultraviolet radiation. Please note the following precautions:

- The mercury spectral lamps emit UV radiation. Do not stare into the lamp. Avoid exposure where possible by switching the lamp off or facing it towards the wall when not in use. **Students and staff must wear safety glasses during the experiment.** The rims of the glasses must be cleaned using the wipes provided before and after use.
- The spectrometer captures light from the lamp and transmits it through an eyepiece. Ensure the entrance slit of the spectrometer is set to a small value ($\ll 1$ mm) before viewing through the eyepiece. Follow the alignment procedure given in the notes.

Further risk assessments are given in the appendix - please read these before starting your experiment.

1 Introduction

Spectroscopy is an important experimental technique used to study the conditions in a radiating gas sample. To do this, the light emitted from the gas is spectrally resolved by a spectrometer and the resulting emission lines are analysed. The simplest spectrum is that of atomic hydrogen, which can be modelled using a semi-classical model proposed by Bohr. For more complex atoms, a completely quantum description is required, and the calculations are computationally expensive. However, it is possible to empirically modify Bohr's model of atomic hydrogen for hydrogen-like alkali atoms.

In this experiment, you will **directly observe optical transitions in a sodium vapour**. You will use a prism spectrometer, which you will first calibrate using the known spectrum of mercury. You should determine the atomic energy levels of the sodium atom, and empirically modify the Bohr model using your results. Finally, you will **quantitatively investigate the spectrum of sodium vapour in a high-pressure lamp**, and explain the physics of any key differences.

2 Background

When an element or salt of an element is heated in a flame, or when an element in the form of a low pressure gas is subjected to an electric discharge, the atoms are excited to higher energy states. They subsequently emit light when they de-excite. The radiation emitted is called the emission spectrum, and contains discrete wavelengths characteristic of the element. Using a spectrometer, a series of bright lines of pure colour is observed on a dark background where each line corresponds to one of these characteristic wavelengths.

2.1 The semi-classical Bohr model

Any successful theory of atomic structure must be able to explain the observed spectral lines for the elements. The spectrum of the hydrogen atom was the first explained on a fundamental basis in the development of atomic physics. In 1885, Balmer found that the frequencies ν of the lines in the visible region of the spectrum of the hydrogen atom were given by the equation

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

where R is the Rydberg constant, c is the speed of light, and n is an integer ($n > 2$). The frequency of the emitted light is related to the wavelength λ by $\nu = c/\lambda$.

The expression developed by Balmer was later generalised to be

$$\nu = Rc \left(\frac{1}{m^2} - \frac{1}{n^2} \right), \quad (2)$$

where m is a positive integer, and $n > m$. This equation was successful in describing all spectral lines of hydrogen. A value of $m = 2$ gives the Balmer series (visible wavelengths), while $m = 1$ is known as the Lyman series (ultraviolet), and $m = 3$ is the Paschen series (infrared).

One early model of atomic structure was based on Thompson's discovery of the electron. In 1898, he proposed a "plum pudding" model of the atom. This was later found to be incorrect following Rutherford's α -particle scattering experiment, which supported the existence of an atomic nucleus. This led to Rutherford to propose a "planetary" atomic model, in which electrons orbit the nucleus. However, classical electromagnetism requires that such an electron would continuously radiate energy, and thereby spiral into the nucleus.

This fundamental difficulty, together with the failure of the model to explain the existence of characteristic spectra, provided the stimulus for Bohr to develop his theory of the atom. The basis of Bohr's theory, from 1913, can be expressed as four postulates:

1. An electron in an atom moves in a circular orbit about the nucleus under the influence of the Coulomb attraction between the electron and the nucleus, and obeys the laws of classical mechanics.
2. Only certain orbits are allowed. It is only possible for an electron to move in an orbit for which its orbital angular momentum L is an integral multiple of the reduced Planck's constant \hbar . That is

$$L = m_e v r = n \hbar = \frac{n h}{2\pi}, \quad (3)$$

where m_e is the mass of an electron, v is its speed, r is the radius of the electron orbit, n is a positive integer, and $\hbar = h/2\pi$. Equation 3 shows that angular momentum is quantised.

3. An electron moving in such an orbit does not radiate electromagnetic energy despite the fact that it is constantly accelerating.
4. Radiation is emitted if an electron initially moving in an orbit of total energy E_i discontinuously changes its motion so that it moves to an orbit of total energy E_f , where $E_f < E_i$. The frequency of the emitted radiation from a single electron is

$$\nu = \frac{E_i - E_f}{h}. \quad (4)$$

Similarly, if $E_i < E_f$, radiation of frequency ν can be absorbed, causing an electron in an orbit of energy E_i to jump to an orbit of energy E_f .

Postulate 1 is based on the idea of an atomic nucleus. Postulates 2, 3 and 4 introduce new ideas, conflicting with classical physics.

The theory presented thus far has assumed that the electron moves about a fixed nucleus. This cannot be correct unless the nucleus is infinitely massive. A refinement to the theory is necessary to account for the fact that the nucleus of mass M , and the electron of mass m_e will rotate about the centre of mass of the two-body system. We introduce the reduced mass μ given by

$$\mu = \frac{m_e M}{m_e + M}. \quad (5)$$

The reduced mass correction introduces a small numerical change in the values for the allowed energies. The mass of an electron is $m_e = 9.11 \times 10^{-31}$ kg. The mass of a proton or neutron is $M = 1.67 \times 10^{-27}$ kg. Using Equation 5, we can see that the reduced mass for hydrogen is $\mu = 9.11 \times 10^{-31}$ kg. As the number of protons and neutrons in the nucleus increases, the reduced mass for a one-electron atom will approach the mass of an electron; the reduced mass correction becomes negligible.

The Bohr model successfully describes the line spectra of the hydrogen atom. However, it does not explain the spectra of other one-electron atoms. Some predicted lines are observed to consist of two or more closely spaced lines. The Bohr model also fails to explain the variation in intensity of different spectral lines. A more complete description of atomic structure was provided by the introduction of quantum mechanics.

2.2 The quantum atomic model

In quantum mechanics, we no longer think of electrons as moving in well-defined orbits. Instead, electrons are thought of as waves, and the behaviour of an electron is described by a wave function Ψ , which can depend on position x and time t . The wave function, unlike a conventional wave, has no physical meaning. However, the expression $\Psi^*\Psi$, where Ψ^* is the complex conjugate of the function Ψ , gives the probability distribution of where the electron may be found.

The wave function satisfies a partial differential equation called a wave equation. If we assume that electrons move in a general spherically symmetric, time-independent potential V , the wave function must satisfy the time independent Schrödinger equation

$$\left(\frac{\hbar}{2\mu}\nabla^2 + V\right)\Psi = E\Psi, \quad (6)$$

where μ is the reduced mass, ∇^2 is the Laplace operator, and E is the total energy. If we solve Equation 6 for a pure Coulomb potential, the energy is the same as in the Bohr model, and is dependent only on the principal quantum number n . The principal quantum number can have the values

$$n = 1, 2, 3, \dots$$

The solution of the Schrödinger equation for a more general potential shows that the energy is given by an expression which is dependent on n and a second quantum number l . This second number is called the orbital angular momentum quantum number as it describes the magnitude of an electron's orbital angular momentum. It can take on the values

$$l = 0, 1, 2, \dots, (n-1).$$

It is customary to specify electron angular momentum states according to the convention

$$l = 0(s), 1(p), 2(d), 3(f), 4(g), \dots$$

A full quantum mechanical treatment of atomic structure reveals two more quantum numbers. The quantum number for the spatial orientation of the orbital angular momentum vector is m_l , and assumes $2l+1$ values over the range

$$m_l = -l, -l+1, \dots, l-1, l.$$

Finally, the intrinsic spin quantum number of the electron is m_s and has just two values of $m_s = \pm 1/2$.

In the general case, electrons with different quantum numbers have different energies. However in some cases, quantum states with different sets of quantum numbers may have the same energy. These energy levels are then called degenerate.

The structure of the electron cloud around the nucleus is described by shells and subshells. Electrons having the same principal quantum number n are said to occupy the same atomic shell. Electrons in a shell that share the same l value are said to occupy the same subshell. A naming convention is used in which each subshell is identified by its principal quantum number n , followed by the letter corresponding to its orbital angular momentum quantum number l . A superscript indicates the number of electrons in that subshell. Hence a subshell $3s^2$ would describe two electrons each having $n = 3$ and $l = 0$. According to the Pauli principle, two electrons cannot occupy the same state defined by n , l , m_l and m_s . Therefore a maximum of $2(2l+1)$ electrons can exist in a subshell.

2.3 The spectrum of alkali atoms

Shells and subshells fill with electrons from the inner shell outwards. A completely filled subshell is spherically symmetric around the atomic core. The outer subshell may only be partially filled depending on the atomic number of the atom. In an alkali element, also called a one electron atom, there is one outer or "valence" electron. Atomic sodium has such an electronic configuration. This is written as

$$1s^2 2s^2 2p^6 3s^1.$$

This means that the $1s$ and $2s$ subshells contain two electrons each, and the $2p$ subshell contains six electrons. These subshells are full. The outer $3s$ subshell contains only one electron.

In an optical excitation of an alkali atom, only the outer electron is excited. The excited states can be described completely by the single, optically active electron. As the closed shells are spherically symmetric, to a good

approximation we can assume that the outer electron is moving in a central field, produced by the nucleus and the other electrons. The presence of these shells however means that the valence electron is no longer moving in a strictly Coulomb field. The energy levels with the same n and different l quantum numbers consequently have different energies. Therefore, the atomic sodium spectrum, as well as the spectrum for any other one-electron atom, will be different from the hydrogen spectrum.

However, it has been *empirically* found that it is possible to modify the expression describing the energy levels of the hydrogen atom to successfully describe the energy levels of one valence electron atoms. In order to establish what modification to this expression is needed, you will experimentally study the spectrum of sodium in detail. From these measurements you will determine how to adapt the expression for hydrogen energy levels to that for sodium.

2.4 Exercises

Include the details of these exercises in the relevant sections of your report:

1. Using Bohr's postulates and classical mechanics, show that the total energy of an electron E_n , with angular momentum $n\hbar$, is proportional to $-1/n^2$. Derive the full expression including relevant constants.
2. Draw a diagram showing the optical paths taken by light of different wavelengths through the spectrometer. Remember that there are collimating lenses in each arm. Explain how and why different wavelengths are dispersed at different angles.
3. Research the choice of letters for the electron angular momentum states (s , p , d , f and g) and see if you can correlate them with your observations.
4. Explain why a plot of $1/\sqrt{-E}$, where E are the energies of sodium, against the principle quantum number n is useful. What quantities can be extracted from such a plot?

3 The experiment

The equipment available for this laboratory consists of a prism spectrometer and three spectral lamps: a low pressure mercury lamp, a low pressure sodium lamp, and a high pressure sodium lamp inside a wooden box.

The spectrometer consists of a prism mounted between two arms. Each arm acts like a telescope. The light first passes through an entrance slit in one arm. This light is collimated by a lens in the arm before striking the prism. The refracted light is then passed to the second arm for observation using an eye-piece.

3.1 Using the equipment

To **align your spectrometer** and view spectral lines:

1. Switch on the low pressure sodium lamp and allow it to warm up for several minutes.
2. Identify the entrance slit of the spectrometer and open it up wide (several millimetres). Place the lamp next to the entrance slit so that light passes into the spectrometer.
3. Use a small sheet of paper to trace the path of the light through the spectrometer – hold it first at the end of the entrance telescope and align the lamp so that a uniform disk of light is observed. Then hold the sheet of paper behind the prism and look for refracted light as you rotate the prism.
4. Optimise the angle, lock down the prism, and note the angle at which the brightest radiation roughly exits the prism.
5. Close down the entrance slit of the spectrometer – close it fully and then open it slightly.
6. Rotate the viewing arm of the spectrometer to the angle that you identified as where the brightest light was transmitted, and look through the eyepiece.

You will have to **optimise the spectrometer** for the intensity and sharpness of the lines. Once complete, you should be able to see spectral lines ranging from red to violet. To do this, try any of the following:

- Change the size of the entrance slit to make the lines narrow, but still visible.
- Rotate the focus knobs for both the viewing telescope and the collimating lens until the lines are in focus.
- Adjust the angle of the viewing telescope to view an interesting region of the spectrum.
- Alter the vertical angle of the prism to ensure the spectral lines are vertical. Do this by twisting one or more of the knobs on the rotating platform.

3.2 Your tasks

Devise a method to calibrate the spectrometer (the readings on the dial only give you angles). You may assume the wavelengths of spectral lines of mercury are well known. These are given in Table 1. The uncertainties in your angle measurements will be larger than uncertainties in these wavelengths – so the latter can be ignored.

Table 1: Mercury Emission Lines

Wavelength (nm)	Colour
404.655	violet
407.781	violet
435.835	blue
491.604	blue/green
546.074	green (bright)
576.959	yellow
579.065	yellow

In Table 2, you will find some of the spectral lines of sodium, and a guide to which lines you will be able to identify and measure. Be aware that other lines may exist due to other gases in the lamp, so you may need to use your analysis to correctly identify them. After all the lines have been recorded, use the results to calculate the energies of each of the levels in the sodium atom. Remember that the spectral lines give you the energy *differences* between levels. You may use the fact that the ground state of sodium ($3s$) has an energy of $E_{3s} = -5.139$ eV (that is, the energy is 5.139 eV below the ionisation limit). In your analysis make use of the lines already quoted in the table which are outside the visible spectrum, so you won't be able to observe them.

Address the following tasks in your analysis of this experiment:

1. Using the energies of the sodium levels E , construct a plot of $1/\sqrt{-E}$ against principal quantum number n . Compare this plot with the earlier expression you derived and use it to determine any relevant constants with uncertainties.
2. By carefully studying your plot and your linear fit, determine how the energy formula derived from the Bohr Model should be modified to be applicable to the spectrum for sodium. (Hint: one thing you may need to do is introduce a constant which is different for different values of l).
3. Construct an energy level diagram called a Grottrian diagram. Indicate on the diagram which transitions you have been able to measure. Does your diagram give you any hints about what rules should be applied to the quantum numbers of the levels involved in the observed transitions?

After you have completed the study of the sodium spectrum using the low pressure spectral lamp, **qualitatively study the spectrum of atomic sodium using a high pressure lamp**. Observe the behaviour of the spectral lines, particularly the bright yellow line, for the first 20 minutes after the lamp is switched on. Comment on your observations.

References

- [1] Carroll, B.W. & Ostlie, D. A. (2014). *An introduction to modern astrophysics* (2nd ed.). Harlow, Essex: Pearson Education Limited.
[Section 6.3 presents a detailed treatment of the Bohr model of the atom. Chapter 6 also contains a useful discussion of Kirchhoff's laws of spectroscopy.]
- [2] Knight, R.D. (2017). *Physics for scientists and engineers: a strategic approach with modern physics* (4th ed.). Boston: Pearson.
[Sections 38.5 to 38.7 outline the Bohr model of quantisation, applying it to the hydrogen atom in a clear and simple way.]
- [3] Kramida, A., Ralchenko, Yu., Reader, J. and NIST ASD Team (2019). NIST Atomic Spectra Database (version 5.7.1), [Online]. Available: <https://physics.nist.gov/asd> [Mon Dec 16 2019]. National Institute of Standards and Technology, Gaithersburg, MD. DOI: <https://doi.org/10.18434/T4W30F>
[A database containing accurate reference spectral lines and atomic energy levels for comparison to your results.]
- [4] Thorne, A.P. (1988). *Spectrophysics* (2nd ed.), Dordrecht: Springer Netherlands.
[Chapter 5 presents a detailed discussion on prism spectrometers such as those used in this experiment.]

Table 2: Sodium Emission Lines

Wavelength (nm)	Transition	Colour
1139	$4s \rightarrow 3p$	infrared
819	$3d \rightarrow 3p$	infrared
	$5s \rightarrow 3p$	red
	$3p \rightarrow 3s$	yellow (bright)
	$4d \rightarrow 3p$	green
	$6s \rightarrow 3p$	green
	$5d \rightarrow 3p$	green
	$7s \rightarrow 3p$	blue-green
	$6d \rightarrow 3p$	blue
	$8s \rightarrow 3p$	violet (weak)
	$7d \rightarrow 3p$	violet (weak)
	$8d \rightarrow 3p$	violet (weak)
	$9s \rightarrow 3p$	violet (weak)
330.24	$4p \rightarrow 3s$	ultraviolet
285.28	$5p \rightarrow 3s$	ultraviolet
268.04	$6p \rightarrow 3s$	ultraviolet

Revised: July 28, 2020