Atomic Spectra

Object: To theoretically and experimentally determine the wavelengths of the emission lines of the Balmer series for atomic hydrogen.

Apparatus: Spectrum tube power supply, mercury and hydrogen emission tubes, diffraction grating, meter stick, two sliding pointers, and associated mounting hardware.

Foreword

Rarefied gases can be excited to emit light. This is accomplished by intense heating or more commonly by applying a high voltage to an emission tube containing the gas at low pressure. Since early in the nineteenth century, the radiation from excited gases has been observed. It was found that the emission spectrum (also called a bright line spectrum) was not a continuous spectrum; it was a discrete spectrum. As a result of the excited gases only emitting light of certain wavelengths, when the light from the excited gases is examined through the slit of a spectroscope or spectrometer, a line spectrum is seen instead of a continuous spectrum. The line spectrums emitted by different elements are unique. Therefore, the emission spectrum is characteristic of the material and it can be used to identify the gas. If a continuous spectrum is passed through a gas, the gas will absorb the wavelengths of light that it usually emits and thus produces an absorption spectrum (also called a dark line spectrum).

It is advisable to start the study of spectra by studying the spectrum of hydrogen. Hydrogen is the lightest atom and has the simplest atomic structure, having only one electron orbiting the nucleus. Hydrogen also happens to have the simplest spectrum. The spacing in the lines of the hydrogen spectrum decreases in an regular way; this is contrary to the spectrum of most atoms which show little apparent regularity. In 1885, Johann Jakob Balmer found that the four visible lines in the spectrum of hydrogen (with measured wavelengths 6562.8 Å, 4861.3 Å, 4340.5 Å, and 4101.7 Å), where $1 \text{ Å} = 1 \times 10^{-10}$ m, would fit the formula

$$(1) \qquad \frac{1}{\lambda} = R \left(\frac{1}{2^2} - \frac{1}{n^2} \right), \quad n = 3, 4, \ldots$$

where n takes the values 3, 4, 5, 6 for the four lines, and R (the Rydberg constant) has the value $R = 1.097 \times 10^7$ m^{-1}. Later it was discovered that this Balmer series of lines extended into the ultraviolet region, with a limit of the series at 3645.6 Å. Balmer's equation, Eq (1), also worked for these lines corresponding to larger integer values of n. The limit of the series at 3645.6 Å corresponds to $n = \infty$.

Experiments later showed that there were similar series of lines in the ultraviolet and infrared regions of the hydrogen spectrum. These other series were found to fit a formula like the Balmer series but with the $1/2^2$ replaced by $1/1^2$, $1/3^2$, $1/4^2$, etc. The Lyman series contains lines with wavelengths between 912 Å and 1216 Å and fits the formula

$$(2) \qquad \frac{1}{\lambda} = R \left(\frac{1}{1^2} - \frac{1}{n^2} \right), \quad n = 2, 3, \ldots .$$

And the lines of the Paschen series fit

$$(3) \qquad \frac{1}{\lambda} = R \left(\frac{1}{3^2} - \frac{1}{n^2} \right), \quad n = 4, 5, \ldots .$$

The Bohr theory predicts that the wavelengths of the emitted photons released when an electron makes a transition from an upper energy level (n_u) to a lower energy level (n_l) may be determined by the formula

(4)
$$\frac{1}{\lambda} = R\left(\frac{1}{m^2} - \frac{1}{n^2}\right).$$

This gives the Balmer series when $m = 2$ and $n = 3, 4, 5$, etc., and the Paschen series when $m = 3$ and $n = 4, 5, 6$, etc.

Equation (4) very precisely represented the entire known hydrogen spectrum at the time, however it was an empirical formula. At this point, we have a correct formula for the hydrogen spectrum, but we still have not derived it. The derivation of this equation was accomplished by Niels Henrik David Bohr in 1913.

Bohr modified Rutherford's theory of the atom. He maintained the small nucleus or core of the atom and suggested that in addition, there were electrons orbiting the nucleus. Bohr maintained that the hydrogen atom had a nucleus consisting of a single proton with one electron orbiting the nucleus. This planetary model of the atom is analogous to the solar system where the heavy positive nucleus is the sun and the light negative electron is like the planet earth. Hydrogen is represented by a tiny one-planet solar system with the electrostatic force of attraction between the oppositely charged particles replacing the gravitational force of the solar system. The gravitational force and the electrostatic force have respectively the general equations

(5)
$$F = G\frac{MM'}{r^2}$$

and

(6)
$$F = \frac{1}{4\pi\varepsilon_0}\frac{qq'}{r^2}.$$

Notice that both forces are inversely proportional to the square of the distance between the particles. In the solar system, the planets have elliptical orbits that are nearly circular. The analysis of the classical mechanics of this problem become straightforward when the assumption is made that the electron of the hydrogen atom travels in a circular orbit. If v is the tangential speed of a mass M' that is revolving around a large mass M in a circular orbit of radius r, revolution occurs about the center of mass of the system which can be taken at the center of the large mass. The gravitational force of attraction due to M results in an centripetal force acting on M'. Therefore, we have

(7)
$$F = G\frac{MM'}{r^2} = M'a = \frac{M'v^2}{r},$$

which leads to

(8)
$$v^2 = \frac{GM}{r}.$$

In the Bohr model of the atom, an electron with mass m_e, charge e, and tangential speed v has a circular orbit of radius r about a massive nucleus with positive charge Ze. Again, the orbital center can be taken at the center of the large nucleus. In this case, the electrostatic force of attraction of the nuclear charge causes the centripetal force acting on the electron. The force equation is then given by

(9)
$$F = \frac{1}{4\pi\varepsilon_0}\frac{(Ze)(e)}{r^2} = m_e a = \frac{m_e v^2}{r}.$$

From equation (9) we can obtain

(10)
$$v^2 = \frac{Ze^2}{4\pi\varepsilon_0 m_e r}.$$

(In the case of hydrogen, the atomic number Z equals one. Z is included for generality.) Equations (8) and (10) both contain a relationship between the tangential speed v and the orbital radius r. Therefore if one of these variables is known, then the other can easily be found. Any pair of values of v and r that satisfy Eq. (8) may actually occur in the gravitational case. Classical physics does not impose any restrictions on the number of solutions that may satisfy Eq. (10) in the electrical case. Bohr imposed a restrictive condition known as the first Bohr postulate on the case of the hydrogen atom. He worked from the assumption that not all the possible orbits that can be calculated from Eq. (10) actually occur in hydrogen. Bohr's first postulate is that *only those orbits occur for which the angular momenta of the planetary electron are integral multiples of h/2π, that is, nh/2π.* Here h is Planck's constant and n is any integer. Mathematically stated the first postulate is

$$(11) \qquad\qquad I\omega = \frac{nh}{2\pi} ,$$

where I is the moment of inertia of the electron about the center, ω is its angular velocity, and n = 1, 2, 3, ... The quantity $I\omega = mr^2\omega = mvr$ for the orbiting electron. We can now state Bohr's first postulate in a very useful form:

$$(12) \qquad\qquad m_e vr = \frac{nh}{2\pi} .$$

Sometimes the product $m_e vr$ is referred to as the moment of momentum of the electron.

Equations (10) and (12) must be simultaneously satisfied by the hydrogen electron. Eliminating v between these equations and solving for r, we find that the only orbits that exist or are "permitted" in the hydrogen atom are those with radii

$$(13) \qquad\qquad r_n = \frac{\varepsilon_0 n^2 h^2}{\pi m_e Z e^2}$$

where the subscript n has been added to denote the radius of the nth orbit. The smallest orbit has n = 1 and for hydrogen (Z = 1) with the value

$$r_1 = \frac{(8.85 \times 10^{-12}\ C^2/N \cdot m^2)(1)^2(6.626 \times 10^{-34}\ J \cdot s)^2}{(3.14)(9.11 \times 10^{-31}\ kg)(1)(1.602 \times 10^{-19}\ C)^2}$$

or

$$r_1 = 0.529 \times 10^{-10}\ m = 0.529\ Å .$$

This smallest radius, r_1, is often referred to as the Bohr radius. From Eq. (13), we see that the radii of the larger orbits increase as n^2, so

$$r_2 = 4r_1 = 2.12\ Å$$

$$r_3 = 9r_1 = 4.76\ Å$$

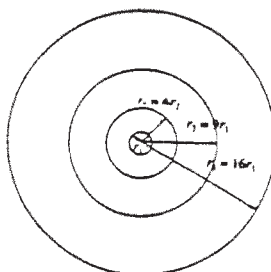and so on. The first four are shown in figure 1.

Figure 1. Possible orbits in the Bohr model of hydrogen.

Now we must turn our attention to the energy of the planetary electron. Since it may seem strange that it proves convenient to consider the electron energy as being negative, let's review some fundamental energy concepts. Only when there is an exchange of energy is it useful to use the energy concept in calculations. Essentially, all energy calculations are the results of integrations that always involve either an initial and a final state (evaluation of a definite integral) or an arbitrary constant (evaluation of an indefinite integral). Therefore we arbitrarily assign a certain energy to a particular state. When considering kinetic energy, we say that a body at rest has no kinetic energy. A man on a moving bus has no kinetic relative to himself, but an observer on the ground regards the man on the bus as moving and having kinetic energy. Each is correct in terms of his arbitrary definition of zero energy. In the case of potential energy, the arbitrary choice of reference level is more familiar. The gravitational potential energy of a mass m is mgy. When this energy is zero, we must specify what is meant by $y = 0$.

We will use the standard convention of field theory when addressing the energy of the planetary electron. Namely, that the electron has no energy when it is at rest infinitely far from its nucleus. Since the electron is capable of doing work as it approaches the positive nucleus, it loses electric potential energy. The electron started at rest at infinity with zero energy; therefore, its potential energy must become negative as it approaches the positive nucleus.

In order to obtain an expression for the electric potential energy of an electron, we realize that the potential at a point which is at a distance r from a nucleus having a charge Ze is

$$(14) \qquad V = \frac{1}{4\pi\varepsilon_0} \frac{Ze}{r} .$$

A negative electronic charge at this point has potential energy $E_p = V(-e)$ or

$$(15) \qquad E_p = -\frac{Ze^2}{4\pi\varepsilon_0 r} .$$

Notice that the potential energy of the electron is negative everywhere except at infinity where it is zero. Using Eq. (10) we find that its kinetic energy is:

$$(16) \qquad E_k = \frac{1}{2} m_e v^2 = \frac{Ze^2}{8\pi\varepsilon_0 r} .$$

Therefore, the total energy of the planetary electron is the sum of the kinetic and potential energies:

$$(17) \qquad E = E_k + E_p = \frac{Ze^2}{8\pi\varepsilon_0 r} - \frac{Ze^2}{4\pi\varepsilon_0 r} = -\frac{Ze^2}{8\pi\varepsilon_0 r} .$$

Now we have the total energy as a function of r. But, remember that that radius r can have only those values that satisfy Eq. (13). Substituting in the value of r from Eq. (13), we find the allowable energy states to be:

$$(18) \qquad E_n = -\frac{m_e e^4 Z^2}{8\varepsilon_0^2 n^2 h^2} ,$$

where $n = 1, 2, 3, \dots$. The integer n is called the total or principle quantum number and it can have any value of the series, 1, 2, 3, ... The value of n restricts the energies of the states. With large values of n, the energy is large, that is, less negative than for small values of n. We refer to the energy required to remove an electron from a particular energy state to infinity as the binding energy of that state. It is numerically equal to E_n.

The energy levels depend on the atomic number Z and the value of n. All the energy levels can be found by multiply the lowest energy level by some factor. This is easily seen if we rearrange Eq. (18) to obtain

$$(19) \qquad E_n = - \frac{m_e e^4}{8 \varepsilon_0^2 h^2} \frac{Z^2}{n^2}.$$

After evaluating all the constants, this simplifies to

$$(20) \qquad E_n = (-2.17 \times 10^{-18} \text{ J}) \frac{Z^2}{n^2} = (-13.6 \text{ eV}) \frac{Z^2}{n^2}$$

For hydrogen, $Z = 1$ and substituting into Eq. (20) we have

$$(21) \qquad E_n = - \frac{13.6 \text{ eV}}{n^2}.$$

Therefore, we have for hydrogen

$$E_1 = - 13.6 \text{ eV},$$

$$E_2 = - \frac{13.6 \text{ eV}}{4} = - 3.40 \text{ eV},$$

and

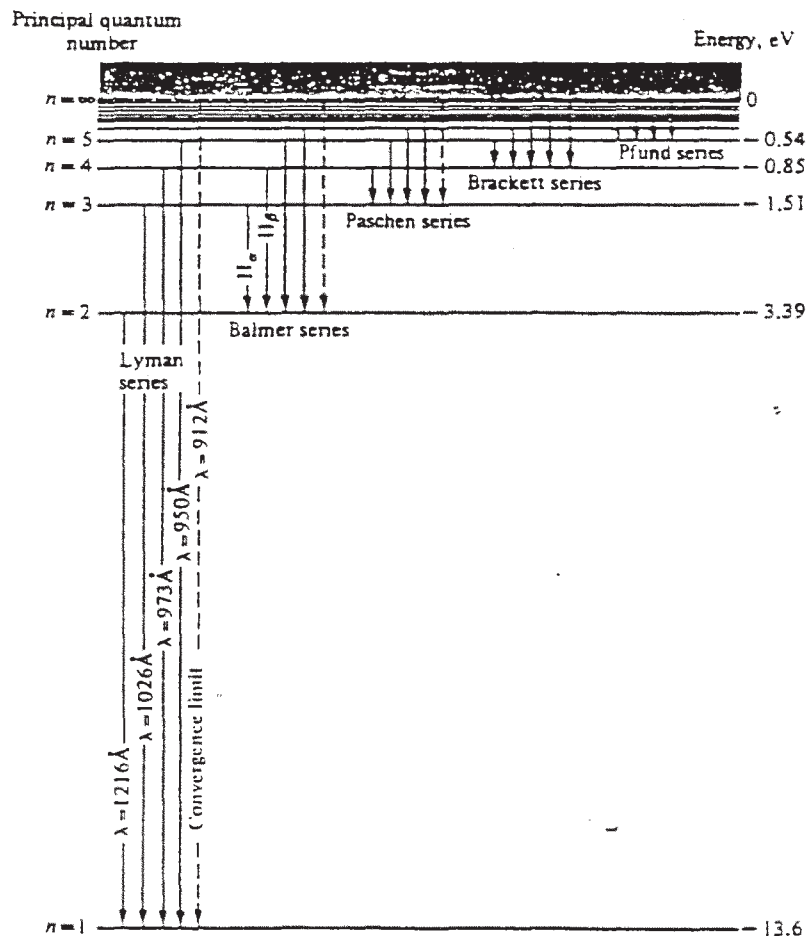$$E_3 = - \frac{13.6 \text{ eV}}{9} = - 1.51 \text{ eV}.$$

Figure 2. Energy-level diagram of the hydrogen atom.

Now we turn our attention to how Bohr attributed the hydrogen spectrum to these energy levels. Classical electrodynamics predicts that if a charged particle is accelerated it will radiate energy. This acceleration can be caused by either a change in direction or a change in speed. Classical theory states that an orbital electron should radiate energy due to its centripetal acceleration. In order for Bohr to preserve his atomic model of planetary electron orbits he had to develop a theory that would violate this classical prediction since, if correct, any electron that was separated from the nucleus would soon radiate away its energy and be drawn into the nucleus. This second break from classical physics by Bohr is contained in his second postulate. Bohr's second postulate states that *no electron radiates energy so long as it remains in one of the orbital energy states; and that radiation occurs only when an electron goes from a higher energy state to a lower one, the energy of the quantum of radiation, $h\upsilon$, being equal to the energy difference of the states.* Letting the quantum number $n = n_u$ represent a higher energy state and $n = n_l$ represent a lower energy state ($n_l < n_u$), Bohr's second postulate can be expressed mathematically as

$$(22) \qquad h\upsilon = E_{n_u} - E_{n_l} .$$

Substituting the energies from Eq. (19), we have

$$(23) \qquad h\upsilon = \left(- \frac{m_e e^4}{8\varepsilon_0^2 h^2} \frac{Z^2}{n_u^2} \right) - \left(- \frac{m_e e^4}{8\varepsilon_0^2 h^2} \frac{Z^2}{n_l^2} \right).$$

Solving for the frequency and simplifying we have

$$(24) \qquad \upsilon = \frac{m_e e^4 Z^2}{8\varepsilon_0^2 h^3} \left(\frac{1}{n_l^2} - \frac{1}{n_u^2} \right)$$

or in terms of the wavelength

$$(25) \qquad \frac{1}{\lambda} = \frac{\upsilon}{c} = \frac{m_e e^4 Z^2}{8\varepsilon_0^2 h^3 c} \left(\frac{1}{n_l^2} - \frac{1}{n_u^2} \right)$$

where c is the speed of light in a vacuum. For hydrogen, $Z = 1$; therefore Eq. (25) becomes

$$(26) \qquad \frac{1}{\lambda} = \frac{m_e e^4}{8\varepsilon_0^2 h^3 c} \left(\frac{1}{n_l^2} - \frac{1}{n_u^2} \right)$$

Now if in Eq. (4) we let $m = n_l$ and $n = n_u$ we have

$$(27) \qquad \frac{1}{\lambda} = R \left(\frac{1}{n_l^2} - \frac{1}{n_u^2} \right).$$

Comparison of Eq. (26) with Eq. (27) shows that they are both of the same form. Furthermore, the constant in the Bohr formulation is the Rydberg constant, R, with value

$$R = \frac{m_e e^4}{8\varepsilon_0^2 h^3 c} = 1.097 \times 10^7 \ m^{-1}.$$

The value of R given here is R_∞, which would be correct if the mass of the electron was infinitely small compared to the mass of the nucleus. If the nucleus' motion is accounted for, m_e must be replaced by the reduced mass. Therefore, $R = R_\infty/(1 + m_e/M)$, where M is the mass of the nucleus. This accounts for the slight variation of R from element to element noted by Rydberg. It is an accomplishment of the Bohr model and theory that the slight variations between the spectra of ordinary hydrogen and its isotope, deuterium (heavy hydrogen), can be attributed to the influence of the nuclear mass. In fact, in 1932, Harold Clayton Urey discovered deuterium spectroscopically.

The Bohr formula yields the Balmer series for $n_l = 2$ and the Paschen series for $n_l = 3$, as we have seen before. However, the Bohr theory places no restrictions on n_l and it suggested that there might be additional hydrogen series not yet experimentally discovered. In 1916, Theodore Lyman found a series in the far ultraviolet, in 1922 Brackett found a new series in the infrared, and in 1924 Pfund found another series in the same region. Table 1 summarizes the five hydrogen series.

Table 1. The spectral series of hydrogen

Values of n_l	Name of series	Values of n_u
1	Lyman	2, 3, 4, ...
2	Balmer	3, 4, 5, ...
3	Paschen	4, 5, 6, ...
4	Brackett	5, 6, 7, ...
5	Pfund	6, 7, 8, ...

In this experiment we will restrict our attention to the visible Balmer series which has $n_l = 2$ and $n_u = 3$ (red), $n_u = 4$ (bluegreen), and $n_u = 5$ (violet).

1.   Place the mercury emission tube in the power supply and then turn it on.   Look at the mercury spectrum through the diffraction grating.   If your vision is good you will be able to see five emission lines (per side) with wavelengths

λ_{red} = 6193 Å

λ_{yellow} = 5780 Å

λ_{green} = 5461 Å

λ_{blue} = 4358 Å

λ_{violet} = 4063 Å.

2.   While looking through the diffraction grating,   record the left (L) and right (R) position of each spectral line that you are able to see.   Determine the average distance from center for each spectral line,   (R - L) / 2.   Turn the power supply off.

3.   Using the data from step 2.,   plot a calibration curve of the wavelength (in Å) vs. the average distance from center (in cm).

4.   Replace the mercury emission tube with the hydrogen emission tube.   Turn the power supply on and look through the diffraction grating.   You should be able to see three spectral lines (per side).   Record the locations and determine the average distance from center as in step 2.   Turn the power supply off.

5.   Using the calibration curve,   determine the wavelengths of the three spectral lines.

6.   Calculate the wavelengths of the spectral lines using the Bohr theory.

7.   Calculate the percent difference between the experimental wavelengths and the wavelengths predicted by the Bohr theory.

DATA AND CALCULATION SUMMARY

Mercury Balmer Series

Color	Wavelength	Location of Spectral Lines		
		Left	Right	Average From Center
Red	6193 Å			
Yellow	5780 Å			
Green	5461 Å			
Blue	4358 Å			
Violet	4063 Å			

Hydrogen Balmer Series

Color	Location of Spectral Lines		
	Left	Right	Average From Center
Red			
Blue-green			
Violet			

Color	n_u	n_l	Wavelength		% Difference
			Bohr theory	From Plot	
Red					
Blue-green					
Violet					