

11.4: Bohr's Theory of the Hydrogen Emission Spectrum

Overview

- To introduce the concept of absorption and emission line spectra and describe the Balmer equation to describe the visible lines of atomic hydrogen.
- Describe Rydberg's theory for the hydrogen spectra.
- Interpret the hydrogen spectrum in terms of the energy states of electrons.

The first person to realize that white light was made up of the colors of the rainbow was Isaac Newton, who in 1666 passed sunlight through a narrow slit, then a prism, to project the colored spectrum on to a wall. This effect had been noticed previously, of course, not least in the sky, but previous attempts to explain it, by Descartes and others, had suggested that the white light became colored when it was refracted, the color depending on the angle of refraction. Newton clarified the situation by using a second prism to reconstitute the white light, making much more plausible the idea that the white light was composed of the separate colors. He then took a monochromatic component from the spectrum generated by one prism and passed it through a second prism, establishing that no further colors were generated. That is, light of a single color did not change color on refraction. He concluded that white light was made up of all the colors of the rainbow, and that on passing through a prism, these different colors were refracted through slightly different angles, thus separating them into the observed spectrum.

Atomic Line Spectrum

The spectrum of *hydrogen*, which turned out to be crucial in providing the first insight into atomic structure over half a century later, was first observed by Anders Angstrom in Uppsala, Sweden, in 1853. His communication was translated into English in 1855. Angstrom, the son of a country minister, was a reserved person, not interested in the social life that centered around the court. Consequently, it was many years before his achievements were recognized, at home or abroad (most of his results were published in Swedish).

Most of what is known about atomic (and molecular) structure and mechanics has been deduced from spectroscopy. Figure 1.4.1 shows two different types of spectra. A continuous spectrum can be produced by an incandescent solid or gas at high pressure ([blackbody radiation](#), for example, is a continuum). An emission spectrum can be produced by a gas at low pressure excited by heat or by collisions with electrons. An absorption spectrum results when light from a continuous source passes through a cooler gas, consisting of a series of dark lines characteristic of the composition of the gas.

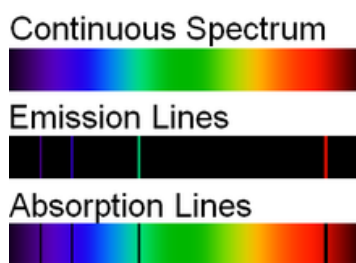


Figure 11.4.1 : Continuous spectrum and two types of line spectra. from Wikipedia.

In 1802, William Wollaston in England had discovered (perhaps by using a thinner slit or a better prism) that in fact the solar spectrum itself had tiny gaps - there were many thin dark lines in the rainbow of colors. These were investigated much more systematically by Joseph von Fraunhofer, beginning in 1814. He increased the dispersion by using more than one prism. He found an "almost countless number" of lines. He labeled the strongest dark lines A, B, C, D, etc. Fraunhofer between 1814 and 1823 discovered nearly 600 dark lines in the solar spectrum viewed at high resolution and designated the principal features with the letters A through K, and weaker lines with other letters (Table 11.4.1). Modern observations of sunlight can detect many thousands of lines. It is now understood that these lines are caused by absorption by the outer layers of the Sun.

Table 11.4.1 : Major Fraunhofer lines, and the elements they are associated with

Designation	Element	Wavelength (nm)
y	O ₂	898.765

Designation	Element	Wavelength (nm)
Z	O ₂	822.696
A	O ₂	759.370
B	O ₂	686.719
C	H	656.281
a	O ₂	627.661
D ₁	Na	589.592
D ₂	Na	588.995
D ₃ or d	He	587.5618

Fraunhofer Absorption Lines

The Fraunhofer lines are typical spectral absorption lines. These dark lines are produced whenever a cold gas is between a broad spectrum photon source and the detector. In this case, a decrease in the intensity of light in the frequency of the incident photon is seen as the photons are absorbed, then re-emitted in random directions, which are mostly in directions different from the original one. This results in an *absorption line*, since the narrow frequency band of light initially traveling toward the detector, has been turned into heat or re-emitted in other directions.

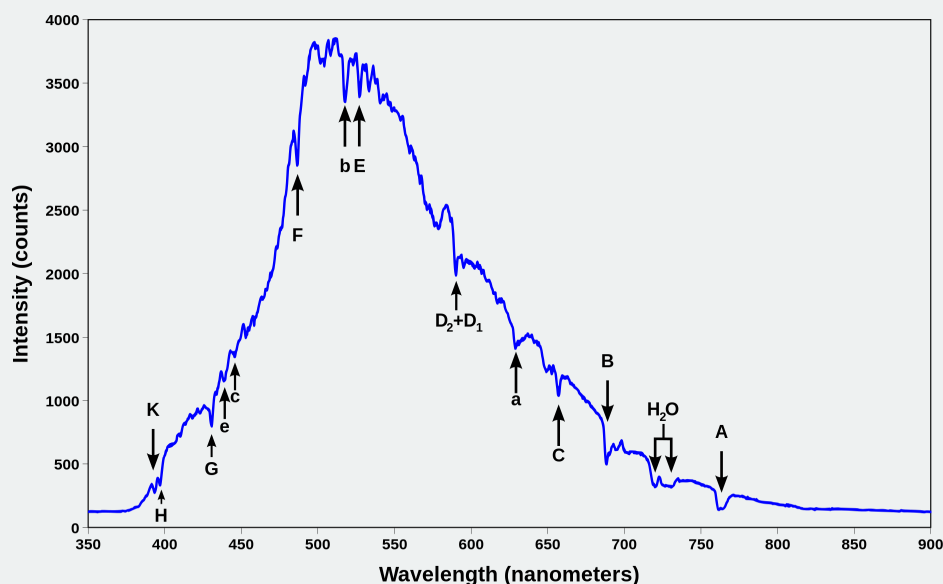


Figure 11.4.2: Spectrum of blue sky. Dips are present at the Fraunhofer line wavelengths. from Wikipedia.

By contrast, if the detector sees photons emitted directly from a glowing gas, then the detector often sees photons emitted in a narrow frequency range by quantum emission processes in atoms in the hot gas, resulting in an *emission line*. In the Sun, Fraunhofer lines are seen from gas in the outer regions of the Sun, which are too cold to directly produce emission lines of the elements they represent.

Gases heated to incandescence were found by Bunsen, Kirkhoff and others to emit light with a series of sharp wavelengths. The emitted light analyzed by a spectrometer (or even a simple prism) appears as a multitude of narrow bands of color. These so called *line spectra* are characteristic of the atomic composition of the gas. The line spectra of several elements are shown in Figure 11.4.3

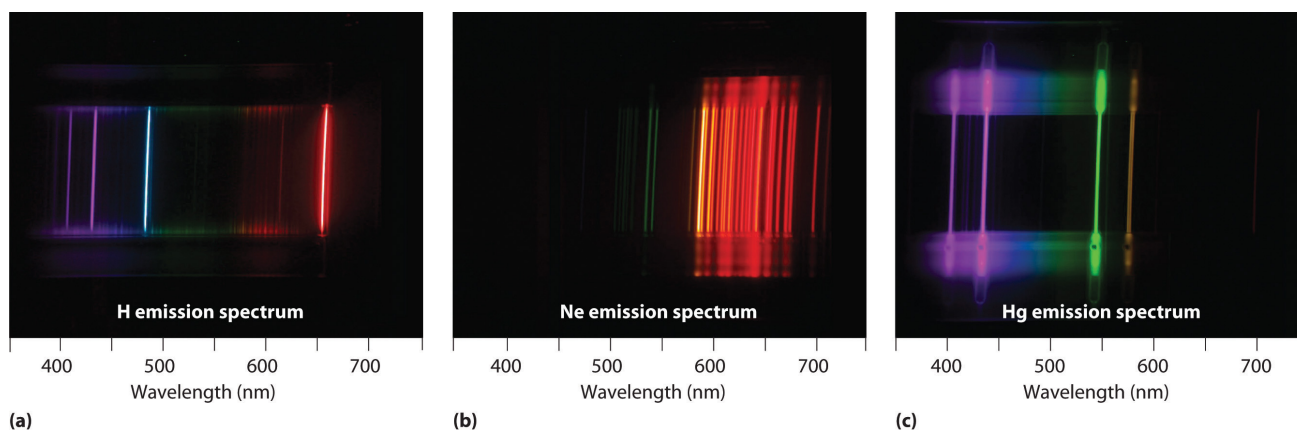


Figure 11.4.3: The Emission Spectra of Elements Compared with Hydrogen. These images show (a) hydrogen gas, which is atomized to hydrogen atoms in the discharge tube; (b) helium; and (c) mercury. The strongest lines in the hydrogen spectrum are in the far UV Lyman series starting at 124 nm and below. The strongest lines in the mercury spectrum are at 181 and 254 nm, also in the UV. These are not shown.

The Balmer Series of Hydrogen

Obviously, if any pattern could be discerned in the spectral lines for a specific atom (in contrast to the mixture that Fraunhofer lines represent), that might be a clue as to the internal structure of the atom. One might be able to build a model. A great deal of effort went into analyzing the spectral data from the 1860's on. The big breakthrough was made by Johann Balmer, a math and Latin teacher at a girls' school in Basel, Switzerland. Balmer had done no physics before, and made his great discovery when he was almost sixty.



Figure 11.4.4: The visible hydrogen emission spectrum lines in the Balmer series. The red line at the right is the H_α line and the two leftmost lines are considered to be ultraviolet as they have wavelengths less than 400 nm. from Wikipedia.

Balmer decided that the most likely atom to show simple spectral patterns was the lightest atom, hydrogen. Angstrom had measured the four visible spectral lines to have wavelengths 656.21, 486.07, 434.01 and 410.12 nm (Figure 11.4.4). Balmer concentrated on just these four numbers, and found they were represented by the formula:

$$\lambda = b \left(\frac{n_2^2}{n_2^2 - 4} \right) \quad (11.4.1)$$

where

- $b = 364.56$ nm and
- $n_2 = 3, 4, 5, 6$.

The first four wavelengths of Equation 11.4.1 (with $n_2=3,4,5,6$) were in excellent agreement with the experimental lines from Angstrom (Table 11.4.2). Balmer predicted that other lines exist in the infrared that correspond to $n = 7, 8$, etc., and in fact some of them had already been observed, unbeknown to Balmer.

Table 11.4.2 : The Balmer Series of Hydrogen Emission Lines

n_2	3	4	5	6	7	8	9	10
λ	656	486	434	410	397	389	383	380
color	red	teal	blue	indigo	violet	not visible	not visible	not visible

The n_2 integer in the Balmer series extends theoretically to infinity and the series resents a monotonically increasing energy (and frequency) of the absorption lines with increasing n_2 values. Moreover, the energy difference between successive lines decreased as n_2 increases (Figure 1.4.4). This behavior converges to a highest possible energy as Example 11.4.1 demonstrates. If the lines

are plot according to their λ on a linear scale, you will get the appearance of the spectrum in Figure 11.4.4 these lines are called the **Balmer series**.

Balmer's general formula (Equation 11.4.1) can be rewritten in terms of the inverse wavelength typically called the *wavenumber* ($\tilde{\nu}$).

$$\tilde{\nu} = \frac{1}{\lambda} = R_H \left(\frac{1}{4} - \frac{1}{n_2^2} \right) \quad (11.4.2)$$

where

- $n_2 = 3, 4, 5, 6$ and
- R_H is the Rydberg constant (discussed below) and is equal to $109,737 \text{ cm}^{-1}$.

He further conjectured that the 4 could be replaced by 9, 16, 25, ... and this also turned out to be true - but these lines, further into the infrared, were not detected until the early twentieth century, along with the ultraviolet lines.

📌 Wavenumbers

The relation between wavelength and frequency for electromagnetic radiation is

$$\lambda \nu = c \quad (11.4.3)$$

In the SI system of units the wavelength, λ is measured in meters (m) and since wavelengths are usually very small one often uses the nanometer (nm) which is 10^{-9} m . The frequency (ν) in the SI system is measured in reciprocal seconds $1/\text{s}$ - which is called a Hertz (after the discover of the [photoelectron effect](#)) and is represented by Hz.

It is common to use the reciprocal of the wavelength in centimeters as a measure of the frequency of radiation. This unit is called a wavenumber and is represented by ($\tilde{\nu}$) and is defined by

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} \quad (11.4.4)$$

Wavenumbers is a convenient unit in spectroscopy because it is directly proportional to energy.

$$E = \frac{hc}{\lambda} \quad (11.4.5)$$

$$E = hc \times \frac{1}{\lambda} \quad (11.4.6)$$

$$E = hc\tilde{\nu} \quad (11.4.7)$$

$$E \propto \tilde{\nu} \quad (11.4.8)$$

✓ Balmer Series

Calculate the longest and shortest wavelengths (in nm) emitted in the Balmer series of the hydrogen atom emission spectrum.

Solution

From the behavior of the Balmer equation (Equation 11.4.1 and Table 11.4.2), the value of n_2 that gives the longest (i.e., greatest) wavelength (λ) is the smallest value possible of n_2 , which is $n_2 = 3$ for this series. This results in

$$\lambda_{\text{longest}} = (364.56 \text{ nm}) \left(\frac{9}{9-4} \right) \quad (11.4.9)$$

$$\lambda_{\text{longest}} = (364.56 \text{ nm}) (1.8) = 656.2 \text{ nm} \quad (11.4.10)$$

This is also known as the H_α line of atomic hydrogen and is bright red (Figure 1.4.4).

For the shortest wavelength, it should be recognized that the shortest wavelength (greatest energy) is obtained at the limit of greatest (n_2):

$$\lambda_{shortest} = \lim_{n_2 \rightarrow \infty} (364.56 \text{ nm}) \left(\frac{n_2^2}{n_2^2 - 4} \right) \quad (11.4.11)$$

This can be solved via [L'Hôpital's Rule](#), or alternatively the limit can be expressed via the equally useful energy expression (Equation 1.4.2) and simply solved:

$$\tilde{\nu}_{greatest} = \lim_{n_2 \rightarrow \infty} R_H \left(\frac{1}{4} - \frac{1}{n_2^2} \right) \quad (11.4.12)$$

$$\tilde{\nu}_{greatest} = \lim_{n_2 \rightarrow \infty} R_H \left(\frac{1}{4} \right) = 27,434 \text{ cm}^{-1} \quad (11.4.13)$$

Since $\frac{1}{\tilde{\nu}} = \lambda$ in units of cm, this converts to 364 nm as the shortest wavelength possible for the Balmer series.

The Balmer series is particularly useful in astronomy because the Balmer lines appear in numerous stellar objects due to the abundance of hydrogen in the universe, and therefore are commonly seen and relatively strong compared to lines from other elements.

The Generalized Rydberg Equation

In an amazing demonstration of mathematical insight, in 1885 Balmer came up with a simple formula for predicting the wavelength of any of the lines in atomic Hydrogen in what we now know as the Balmer series (Equation 11.4.2). Three years later, Rydberg generalized this so that it was possible to determine the wavelengths of any of the lines in the hydrogen emission spectrum. Rydberg suggested that all atomic spectra formed families with this pattern (he was unaware of Balmer's work). It turns out that there are families of spectra following Rydberg's pattern, notably in the alkali metals, sodium, potassium, etc., but not with the precision the hydrogen atom lines fit the Balmer formula, and low values of n_2 predicted wavelengths that deviate considerably.

Rydberg's general equation is as follows:

$$\tilde{\nu} = \frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad (11.4.14)$$

where

- R_H is the *Rydberg* constant and is equal to $109,737 \text{ cm}^{-1}$.
- n_1 and n_2 are integers (whole numbers) with $n_2 > n_1$.

For the Balmer lines, $n_1 = 2$ and n_2 can be any whole number between 3 and infinity. The various combinations of numbers that can be substituted into this formula allow the calculation the wavelength of any of the lines in the hydrogen emission spectrum; there is close agreement between the wavelengths generated by this formula and those observed in a real spectrum.

Other Series

The results given by Balmer and Rydberg for the spectrum in the visible region of the electromagnetic radiation start with $n_2 = 3$, and $n_1^2 = 2$. Is there a different series with the following formula (e.g., $n_1 = 1$)?

$$\frac{1}{\lambda} = R_H \left(\frac{1}{1^2} - \frac{1}{n^2} \right) \quad (11.4.15)$$

The values for n_2 and wavenumber $\tilde{\nu}$ for this series would be:

Table 11.4.3: The Lyman Series of Hydrogen Emission Lines ($n_1 = 1$)

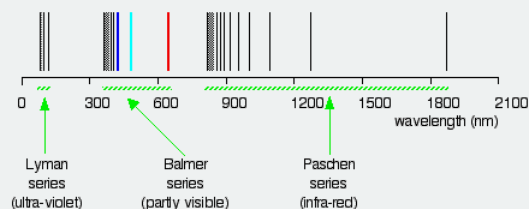
n_2	2	3	4	5	...
λ (nm)	121	102	97	94	...
$\tilde{\nu}$ (cm ⁻¹)	82,2291	97,530	102,864	105,332	...

These lines are in the UV region, and they are not visible, but they are detected by instruments; these lines form a **Lyman series**. The existences of the Lyman series and Balmer's series suggest the existence of more series. For example, the series with $n_2^2 = 3$ and $n_1^2 = 4, 5, 6, 7, \dots$ is called **Paschen series**.

Note

The spectral lines are grouped into series according to n_1 values. Lines are named sequentially starting from the longest wavelength/lowest frequency of the series, using Greek letters within each series. For example, the ($n_1 = 1/n_2 = 2$) line is called "Lyman-alpha" (Ly- α), while the ($n_1 = 3/n_2 = 7$) line is called "Paschen-delta" (Pa- δ). The first six series have specific names:

- Lyman series with $n_1 = 1$
- Balmer series with $n_1 = 2$
- Paschen series (or Bohr series) with $n_1 = 3$
- Brackett series with $n_1 = 4$
- Pfund series with $n_1 = 5$
- Humphreys series with $n_1 = 6$



The spectral series of hydrogen based of the Rydberg Equation (on a logarithmic scale).

✓ Example 11.4.2: The Lyman Series

The so-called Lyman series of lines in the emission spectrum of hydrogen corresponds to transitions from various excited states to the $n = 1$ orbit. Calculate the wavelength of the lowest-energy line in the Lyman series to three significant figures. In what region of the electromagnetic spectrum does it occur?

Given: lowest-energy orbit in the Lyman series

Asked for: wavelength of the lowest-energy Lyman line and corresponding region of the spectrum

Strategy:

- Substitute the appropriate values into Equation 1.5.1 (the Rydberg equation) and solve for λ .
- Locate the region of the electromagnetic spectrum corresponding to the calculated wavelength.

Solution:

We can use the Rydberg equation to calculate the wavelength:

$$\frac{1}{\lambda} = \mathfrak{R} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad (11.4.16)$$

A For the Lyman series, $n_1 = 1$.

$$\frac{1}{\lambda} = \mathfrak{R} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = 1.097 \times m^{-1} \left(\frac{1}{1} - \frac{1}{4} \right) = 8.228 \times 10^6 m^{-1} \quad (11.4.17)$$

Spectroscopists often talk about energy and frequency as equivalent. The cm^{-1} unit is particularly convenient. The infrared range is roughly $200 - 5,000 \text{ cm}^{-1}$, the visible from $11,000$ to $25,000 \text{ cm}^{-1}$ and the UV between $25,000$ and $100,000 \text{ cm}^{-1}$. The units of cm^{-1} are called wavenumbers, although people often verbalize it as inverse centimeters. We can convert the answer in part A to cm^{-1} .

$$\tilde{\nu} = \frac{1}{\lambda} = 8.228 \times 10^6 \text{ m}^{-1} \left(\frac{m}{100 \text{ cm}} \right) = 82,280 \text{ cm}^{-1} \quad (11.4.18)$$

and

$$\lambda = 1.215 \times 10^{-7} \text{ m} = 122 \text{ nm} \quad (11.4.19)$$

This emission line is called Lyman alpha. It is the strongest atomic emission line from the sun and drives the chemistry of the upper atmosphere of all the planets producing ions by stripping electrons from atoms and molecules. It is completely absorbed by oxygen in the upper stratosphere, dissociating O₂ molecules to O atoms which react with other O₂ molecules to form stratospheric ozone

B This wavelength is in the ultraviolet region of the spectrum.

? Exercise 11.4.2: The Pfund Series

The Pfund series of lines in the emission spectrum of hydrogen corresponds to transitions from higher excited states to the $(n_1 = 5)$ orbit. Calculate the wavelength of the *second* line in the Pfund series to three significant figures. In which region of the spectrum does it lie?

Answer: $4.65 \times 10^3 \text{ nm}$; infrared

The above discussion presents only a phenomenological description of hydrogen emission lines and fails to provide a probe of the nature of the atom itself. Clearly a continuum model based on classical mechanics is not applicable.

Contributors and Attributions

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