

Atomic Spectroscopy

The Electromagnetic Spectrum

The electromagnetic spectrum is the classification of electromagnetic waves by energy. (Spectrum in Latin means 'appearance'.)

Visible light is only a small fraction of the energy that surrounds us every day.

We are also surrounded by invisible light-like waves, which together with visible light make up the electromagnetic spectrum.

Electromagnetic waves are invisible and can travel through a vacuum. They do not need particles in order to travel.

Electromagnetic waves do not require a material medium for transmission, as can be seen by the fact that we receive visible light from the sun through the vacuum of space.

Electromagnetic waves involve electric and magnetic fields that can travel through empty space.

The electromagnetic spectrum is a diagram that illustrates the range, or spectrum, of electromagnetic waves, in order of wavelength or frequency.

The **frequency** of a wave is the number of waves that pass a point per unit of time, symbolized by the letter, f (or the Greek letter nu, ν).

Wavelength is the distance between similar points in a set of waves, such as from crest to crest or trough to trough.

Electromagnetic waves differ from each other by wavelength and frequency. The waves can be ordered by increasing frequency on a continuum or spectrum.

Examples of electromagnetic waves are: radio waves, microwaves, infrared, visible light, ultraviolet, X-rays and gamma rays. This is simply a traditional naming scheme, in reality there is smooth gradation from one region to another. Radio waves have the longest wavelength and gamma rays are the shortest. Each electromagnetic wave has its own wavelength and frequency.

The waves that make up the electromagnetic spectrum are classified in terms of *frequency* and *wavelength*, as shown in the spectrum below. *Energy increases as frequency increases.*

High energy: _____ frequency, _____ wavelength.

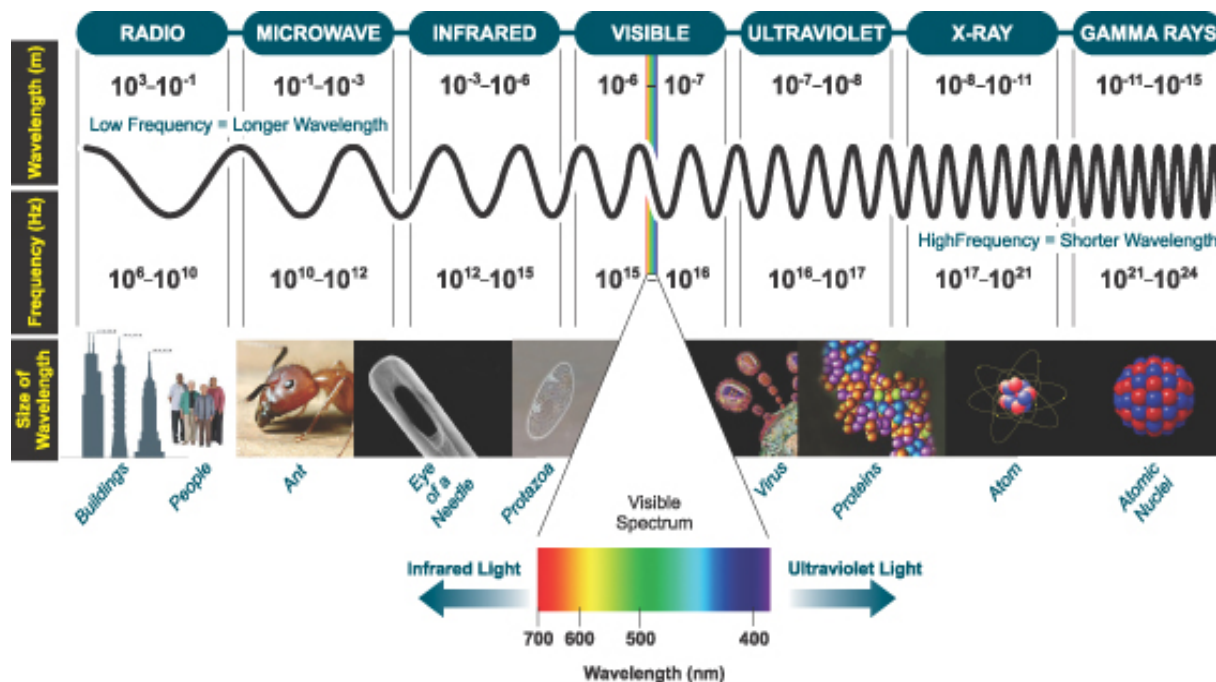
Low energy: _____ frequency, _____ wavelength.

A mathematical relationship exists between wavelength and frequency for any electromagnetic wave:

$$c = f \lambda$$

The speed of light in a vacuum, c , $2.9979 \times 10^8 \text{ ms}^{-1}$, is one of the fundamental constants of nature and doesn't vary with the wavelengths or any other properties of light.

The Electromagnetic Spectrum



Visible light spectrum

The light that we can see forms a very small part of the electromagnetic spectrum — the visible spectrum.

The visible spectrum consists of the wavelengths that the eye can detect.

The visible portion of the spectrum has been expanded in the above diagram to show the range of colours:

White light is formed by different colours: ROYGBIV. Wavelengths of the visible region of the spectrum are from 350 to 750 nm (violet to red : short to long wavelength).

Each coloured ray has its characteristic wavelength and frequency.

There are other rays that can be detectable but not visible.

All the rays form the ELECTROMAGNETIC SPECTRUM

Radio, Waves, TV Waves	Micro-waves, Radar, Sonar	infra-Red	Visible light	Ultra-Violet	X-Rays	γ -rays
------------------------	---------------------------	-----------	---------------	--------------	--------	----------------

Long waves -----> Short Waves

Low Frequency -----> High Frequency

Low Energy -----> High Energy

The Bohr Model of the Atom

Although the mass of an atom is concentrated in the nucleus, it is the electrons which are largely responsible for chemical behaviour.

Once the existence of the nucleus was established, models of the atom began to concentrate on the electron configuration of an atom (i.e. the arrangements of electrons around the nucleus) to try to provide clues to the chemical behaviour of atoms.

Bohr proposed that electrons could possess only specific quantities of energy called **quanta** (singular is **quantum**).

Each specific quantity corresponded to a specific energy level located a particular distance from the nucleus.

Bohr identified each energy level using an integer, n , called the **principal quantum number**.

This number could have any whole-number value from one to infinity.

The larger the value of n , the further from the nucleus is the energy level and the greater the energy associated with the electron.

In the diagram below, the single electron of hydrogen is represented by an arrow.

The electron normally remains in the lowest energy level ($n = 1$).

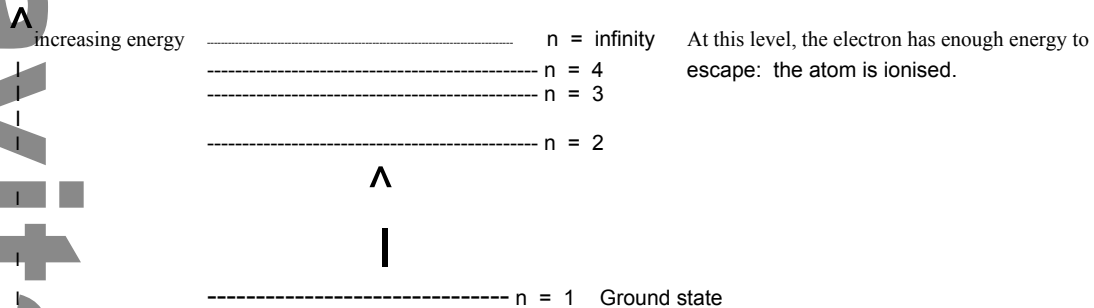
When in its lowest energy level, the electron is said to be in its **ground state**.

If energy is added to the atom, the electron may absorb enough energy to move to a higher energy level.

The electron is then said to be in an **excited state**.

When the electron falls back to lower energy levels it emits energy in the form of light.

(This is why each element has a **characteristic line spectrum**.)



The principal energy levels of the hydrogen atom come closer together as the value of the principal quantum number, n , increases from 1 to infinity.

An atom radiates energy only when the electron jumps from one allowed state to a lower one.

An excited electron drops to a lower energy level and emits radiation of a certain frequency.

This frequency depends on the size of the jump as well as the final level that the electron reaches.

The principal energy levels of the hydrogen atom come closer together as the value of the principal quantum number, n , increases from 1 to infinity.

Bohr proposed that the electron configurations of atoms with more than one electron follow the same pattern as is shown above for hydrogen.

He also outlined two rules that apply as electrons are added to different energy levels:

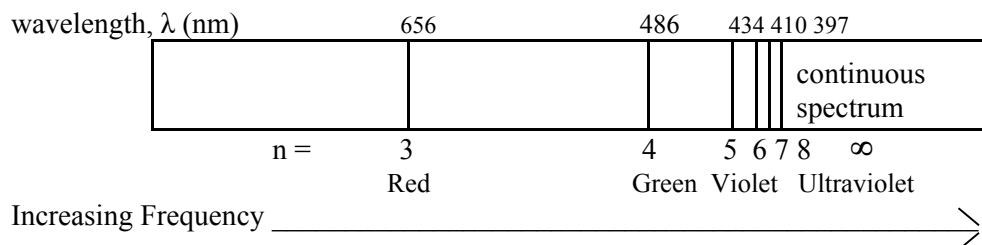
1. Additional electrons always occupy the lowest available energy level.
2. The maximum number of electrons that can be placed in any particular energy level is given by the formula:

$$\text{maximum no. of electrons} = 2n^2 \quad n = \text{the value of the principle quantum number}$$

The frequencies of the colored lines in the visible spectrum of hydrogen matched perfectly with the theory.

Bohr's atomic model gained credibility when he was able to predict lines outside the visible region (ultraviolet).

Hydrogen Line Spectra



Atomic Emission Spectra: Line Spectrum

The spectra produced by certain gaseous substances, consists of only a limited number of coloured lines with dark spaces between them.

See the Hydrogen Line Spectra above

These discontinuous spectra are called **atomic or line spectra**.

Each element has its own distinctive line spectrum – a kind of atomic fingerprint, this regularity in the line spectra was the key to understanding electronic structure.

Each element has a **characteristic line spectrum**

The most extensively studied atomic spectra is that of hydrogen. Hydrogen is the simplest of the atoms, consisting of a single proton and a single electron.

The emission spectrum of hydrogen is of interest because this spectrum was the first to be completely explained by a theory of atomic structure, by the scientist Niels Bohr.

Atoms absorb and emit radiation as light of fixed, characteristic wavelengths when excited. This absorption and emission of light is now known to correspond to electrons within the atom moving away from the nucleus (energy absorbed) or closer to the nucleus (energy emitted).

Atoms emit and absorb energy of only certain wavelengths (bright or dark lines in the spectrum) because electrons don't move randomly away from and toward the nucleus, but may only move between certain fixed, allowed "orbitals", each of which is at a definite distance from the nucleus.

When an electron moves from one of the fixed orbitals to another orbit, the attractive force of the nucleus changes by a definite amount that corresponds to a specific change in energy.

Max Planck is the originator of the "quantum idea". In 1900 while trying to explain the mystery of the black body radiation, Planck discovered: $E = hf$, as the energy representing the black body radiation.

In 1900, Max Planck studied the emissions of light from hot, glowing solids. He observed that the colour of the solid varied with temperature. Planck suggested a relationship between the energy of atoms in the solid and the wavelength of light being emitted.

Planck suggested the energy values of the atoms varied by small whole numbers, "packets" of energy; and that the *energy was proportional to the frequency of the light wave.*

These packets of energy became known as **photons** by Einstein. Einstein found that light impinging on a clean metal surface caused the surface to emit electrons (hence the word "**photoelectric effect**"). The energy of the emitted electrons was directly proportional to the frequency of the light aimed at the metal. He explained this effect by explaining that light consisted of discrete particles, or **photons**, of energy, with each photon possessing an energy equal to Planck's constant times the frequency of the light, f .

$$E = hf$$

The energy of a photon is given by the Planck equation:

$$E = hf \quad E = hc/\lambda \quad c = f\lambda$$

where ' f ' is the frequency of light emitted or absorbed

λ is the wavelength (m), corresponding to that frequency, (frequency has units of cycles per seconds, since cycles is a dimension-less quantity, the unit is written s^{-1} , reciprocal seconds. In the SI system one cycle per second is a hertz, Hz, $1 \text{ Hz} = 1 \text{ s}^{-1}$)

h is the Planck's constant, it has the units of *energy x time*, and has a value of $6.626 \times 10^{-34} \text{ J s}$.

A quantum of radiant energy is called a **photon**, and each photon has energy, $E = hf$.

(Quanta is the plural of quantum.)

The energy of a particular quantum is indicated by the wavelength (or frequency) of the light emitted or absorbed by the atom.

Each frequency of light has its own specific energy per photon. Light is said to be **quantized**.

Thus energy, in whatever form is "**quantized**" i.e. finite, small packets.

Something that is **quantized** is restricted to amounts that are whole-number multiples of the basic unit, or quantum, for the particular system; energy exists only in discrete amounts called quanta (the energy of a photon).

A whole-number multiplier that specifies an amount of energy (or anything else that is quantized) is called a **quantum number**.

A quantum is like a package or bundle of something that is available only in specific and separate amounts. A quantum is somewhat like the scoops of ice cream, you can order one scoop, or two scoops, but not 1.5 or 2.35 scoops. The amount of ice cream that you can get is "n" times the size of the scoop. (Other items that come in quantized packets: raisins, paperclips, staples.)

Quantum theory is a general term for the idea that energy is quantized and the consequences of that idea. The quantity of energy absorbed or emitted by an electron in moving from one allowed orbit to another is called a **quantum (photon)**

Bohr postulated that the energy of an electron when it is in a particular orbit was given by the formula:

$$E_n = - \frac{\text{constant}}{n^2} = \frac{R_H}{n^2}$$

where n is the number of the orbit as counted out from the nucleus ($n = 1$ means the first orbit, $n = 2$ means the second orbit, etc.) and is called the *principle quantum number*.

The proportionality constant in Bohr's theory is called the **Rydberg constant** (given the symbol R_H) and has the value $2.179 \times 10^{-18} \text{ J}$.

The electron energy value becomes negative, with its value lowered, energy has been released.

According to Bohr's theory, if an electron were to move from an outer orbit (designated as n_{outer}) to an inner orbit (designated by n_{inner}), a photon of light should be emitted, having energy given by:

$$\Delta E = E_{\text{inner}} - E_{\text{outer}} = -R_n \left(\frac{1}{n_{\text{inner}}^2} - \frac{1}{n_{\text{outer}}^2} \right)$$

The wavelength, λ of this photon would be given by the Planck's formula as:

$$\lambda = \frac{hc}{\Delta E}$$

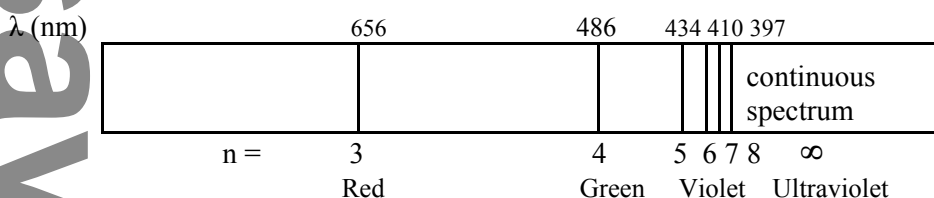
The Atomic Emission Spectrum of Hydrogen

The spectral lines observed in the visible spectrum of hydrogen arise from transitions from upper states back to the $n = 2$ principal quantum level.

Calculate the predicted wavelengths for the spectral transitions of the hydrogen atom from the:

$$\begin{array}{l} n = 6 \longrightarrow n = 2 \\ n = 5 \longrightarrow n = 2 \\ n = 4 \longrightarrow n = 2 \\ n = 3 \longrightarrow n = 2, \text{ levels in atomic hydrogen.} \end{array}$$

These transitions to the $n = 2$ level are referred to as the *Balmer Series* of lines in the spectrum, as shown in the diagram below:



Because the differences between energy levels are limited in number, so are the energies of the emitted photons.

Therefore only certain wavelengths (or frequencies) are observed for the spectral lines, thus **discrete lines**.

The intervals between the frequencies of the lines become smaller and smaller towards the high frequency end of the spectrum until the lines run together or **converge** to form a continuum of light.

Bohr used Einstein's idea of photon of energy to explain the specific amounts of energy observed in hydrogen's bright line spectrum.

Further, when Bohr used his calculations to find the energy levels of hydrogen, his values for the spectral lines matched the mathematical relationship found by Johann Balmer.

Bohr performed calculations of wavelengths for various values of the principal quantum number, n , and found that the predicted wavelengths from theory agreed exactly with experimental wavelengths measured with a spectroscope.

Bohr even went so far as to predict emissions by hydrogen atoms in other regions of the electromagnetic spectrum (ultraviolet, infrared) that had not yet been observed experimentally but that were confirmed almost immediately.

In addition to the visible lines in the hydrogen emission spectrum, atomic hydrogen also emits short-wavelength ultraviolet radiation (for example, sunburns are a result of such radiation from the sun). Ultraviolet emissions arise from transitions back to the ground state ($n = 1$) – this is referred to as the *Lyman Series*.

The hydrogen spectrum consists of five series of lines, named for the men who discovered them. The first interpretation of the hydrogen spectrum was an empirical one based on the observed spectrum, Lyman ($n = 1$), Balmer ($n = 2$), Paschen ($n = 3$), Brackett ($n = 4$), Pfund ($n = 5$).

Bohr's simple atomic theory of an electron moving between fixed orbits helped greatly to explain observed spectra and formed the basis for the detailed modern atomic theory for more complex atoms with more than one electron.

Drawbacks to Bohr's Theory

The notion of negative electrons orbiting a positively charged nucleus does not work, since an accelerating charge would emit continuously, lose energy and fall into the nucleus.

This theory only worked for hydrogen, and for no other element.

The spectra of larger atoms are considerably more complicated than that of hydrogen, but generally a characteristic spectrum is seen.

When applied to multi-electron atoms, several series of lines were seen that should not have been there. These extra lines were given names: **Sharp, Principle, Diffuse, Fundamental**

Bohr was also wrong in thinking that an electron's position and motion can be specified at a given time, as well as thinking that orbits have fixed radii.

A number of common metallic elements emit light strongly in the visible region when ions of the metals are excited.

A number of metallic elements from Groups I and II have especially bright emission lines in the visible light region.

The emissions are so strong and characteristically coloured that these elements can often be recognized by the colour they impart when aspirated into a burner flame.

For example, Li^{+1} impart a red colour, Na^{+1} , a yellow/orange colour, K^{+1} a violet colour, Ca^{2+} a brick red colour, Sr^{2+} , a brighter red colour, Ba^{2+} a green colour.

Upon examination with the spectroscope, it is noted that the spectra of these ions contain several additional lines, but generally the brightest line in the spectrum corresponds to the colour imparted to a flame. The fact that atoms could give off distinct spectra has many applications:

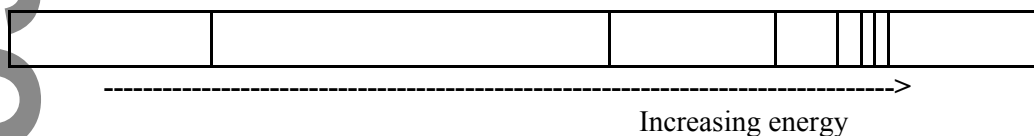
Neon signs, sodium lamps, mercury lamps, flares, calcium oxide used to light theater stage
Identifying elements; spotting of chemicals in space from their spectra

(The red lights of many advertising signs are produced by discharge lamps containing the gas neon, and orange street lamps are discharge tubes containing sodium vapour.)

One of the lines in the spectrum of caesium is used to define the unit of the second. The light from this line has 9.192×10^9 vibrations per second.

Assignment

1. The following diagram represents the atomic emission spectrum of hydrogen.



- Explain why it is composed of lines, and say what each line indicates.
 - Why do the lines become closer together as you read from left to right?
 - state in which direction frequency increases.
 - What do the transitions in these series all have in common?
 - Explain how the lines in the emission spectrum of hydrogen are related to the energy levels of electrons.
- Beginning with the $n = 6$ level, calculate the wavelengths for the ultraviolet emissions of atomic hydrogen.
 - Complete Assignment: Quantum Mechanics Calculation**