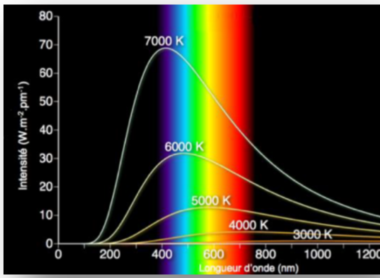
The electron cloud

Introduction to spectroscopy

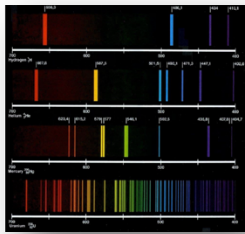
1. SPECTRUM AND TEMPERATURE



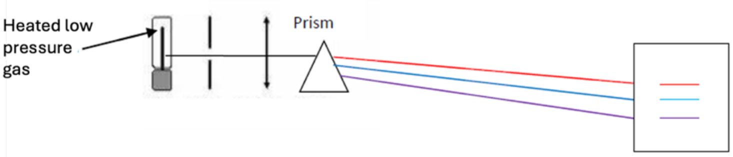
When heated, a gas at high pressure emits light. This is called thermal emission.
The spectrum of the light emitted is continuous.
When the temperature of the gas increases, so does the intensity of the light emitted, with a color switching gradually from red to white. Its spectrum becomes richer in short wavelength radiations.
The color of the radiations emitted by a heated gas, and therefore its spectrum, depend on the temperature of this gas.
This dependence is given by Wien's Law: $\lambda_{max} = \frac{2.9\times10^{-3}}{T}$

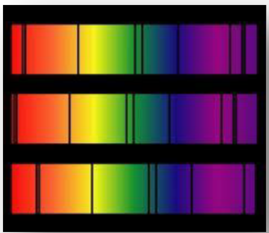
2. LINE SPECTRUM

- ***emission of light by a gas at low pressure***



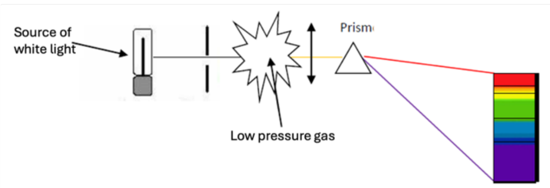
A low-pressure gas emits light when heated, but its spectrum is not continuous. It is made up of individual colored lines corresponding to discontinuous monochromatic emitted radiation, depending on the chemical species contained in the gas. Such a spectrum is called an emission line spectrum



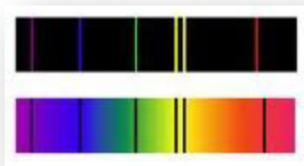


- ***Absorption of light by a low pressure gas***

When white light travels through low-pressure gas, some of the radiations are absorbed. A "continuous » spectrum with dark lines can be observed. These lines correspond to missing monochromatic radiations, that have been absorbed by the elements constituting the gas. Such a spectrum is called an absorption line spectrum.



- ***line spectrum and elements***



The black lines of the absorption spectrum of an element are exactly on the same relative position than the colored lines of the emission spectrum of this element. An element can only absorb the radiations that it can emit, and an element can be studied through the analysis of either its emission spectrum or its absorption spectrum.
No two elements have the same spectrum. Therefore, it is its signature.
Spectroscopy uses this to identify the presence of elements in the structure of distant stars and planets, by comparing the spectrum of the light coming from them to the known spectra of the elements.

Note: Helium has been discovered this way. The absorption spectrum of the Sun (observed by German scientist Joseph Fraunhofer, then interpreted by Robert Bunsen and Gustav Kirchoff) had a few unidentified dark lines. French scientist Jules Janssen proposed an explanation to these unsolved lines by the existence of a new element he called Helium (from Helios, the Sun)

A quantic approach to explain all this

Spectroscopy is a great exploratory tool, but it has several theoretical issues:

- The existence of objects of different colors yet at the same temperature contradicts Wien's law, and therefore a wave description of light.
- And nobody has any clue about all those lines.

Another explanation must therefore be found for the origin of the color of these objects.

1. Light is « made of » particles

In 1905, physicist Albert Einstein explained the photoelectric effect by postulating that energy transfers between matter and light are not continuous, but quantized.

According to him, energy radiated in the form of a wave of frequency υ can be associated with the emission of energy particles called photons.

Each photon, a massless particle, has an energy E_{ph} given by Planck's relation:

$$\mathbf{E_{ph} = h\upsilon = h\frac{c}{\lambda}}$$

2. Quantification of the energy of an atom

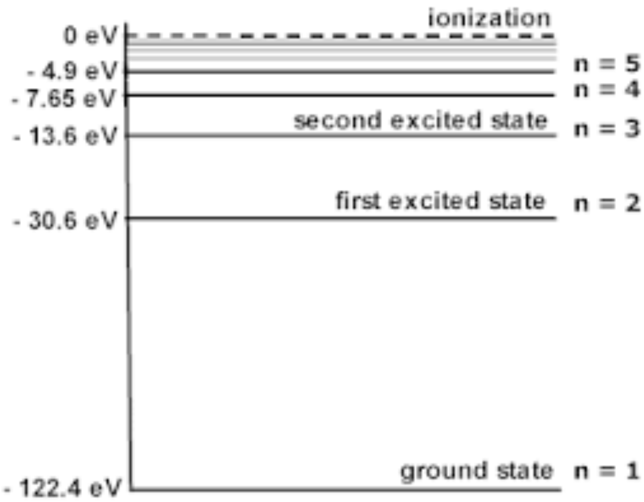
In 1913, Danish physicist Niels Bohr proposed a quantum model of the atom:

An atom can only exist in well-defined states (corresponding to well-defined distributions of electrons in electron shells), each of which is characterized by an energy level. The energy states of the atom are therefore quantized.

Ex: *For hydrogen, $E_n = -\frac{13.6}{n^2}$, in eV, n being an integer number. The formula becomes more complicated for atoms with more than one electron, as the interactions between electrons need to be taken in account.*

The lowest energy state (n = 1) corresponds to the ground state of the atom. It is therefore stable.

The other states (n = 2, 3, 4, ...), with higher energies, correspond to excited states.



Notes:

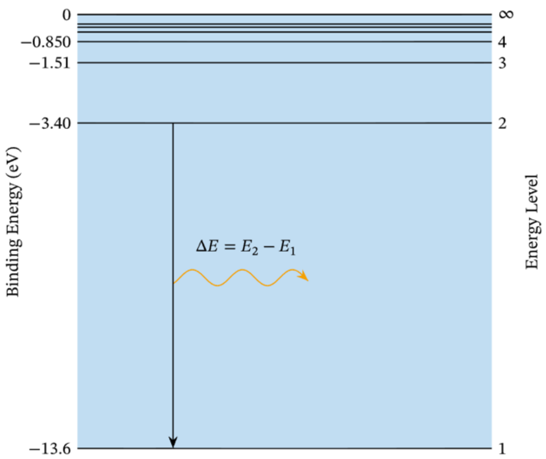
- *The gaps between energy levels become smaller with increasing values of n. The energy levels converge at higher energies.*
  The convergence limit corresponds to ionization: the atom looses an electron. (HL)
- *When an atom is ionized in the form of a cation, the energy binding the lost electron to the atom is zero. The energy levels of the atom therefore have negative values. The energy needed to ionize the atom is called ionization energy. First ionization energy corresponds to the energy needed to lose the first electron, second ionization energy corresponds to the energy needed to lose the second electron, ...*

3. A quantized atom absorbs/emits light

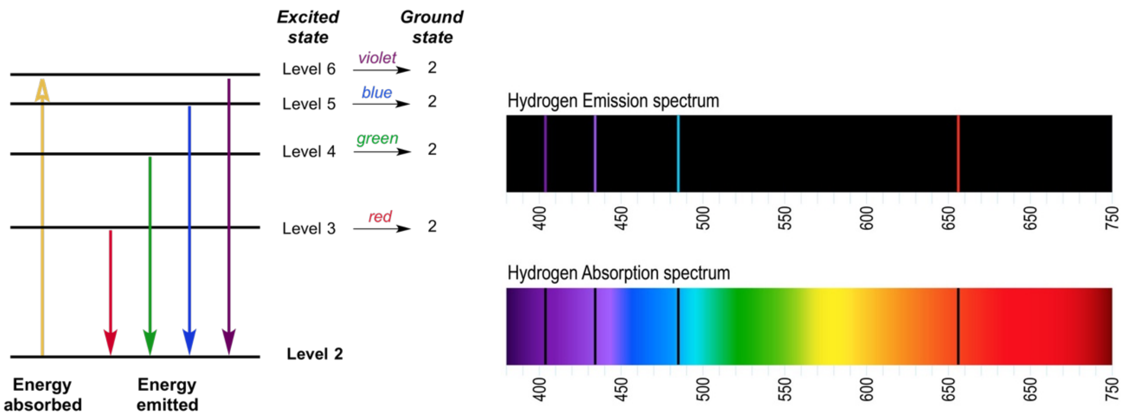
When interacting with its environment, an atom moves from one energy level to a higher energy level by gaining energy: One of its electrons then moves from one electron shell to a higher energy electron shell. Similarly, energy can be lost to move to a lower level.
These processes are called transitions.

Note: A transition can take place ONLY if the atom receives/loses the exact energy needed for the transition

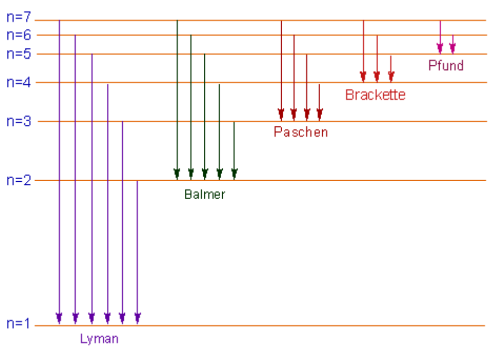
The atom then emits a photon of energy $\mathbf{E_{ph}} = \Delta\mathbf{E} = \mathbf{E_{final}} - \mathbf{E_{initial}}$. This photon has a wavelength $\boldsymbol{\lambda} = \frac{\mathbf{hc}}{|\Delta\mathbf{E}|}$



Ex: Link between the transitions for the hydrogen atom and its spectra.



Note: Only the transitions corresponding to visible light are represented above. Most of the transitions for hydrogen occur in UV or IR.



Electron configuration of an atom

The electrons in an atom do not all have the same energy. They are distributed around the nucleus in correspondingly energetic **layers** (also called shells) and sublayers according to Klechkowski's rule.

KLECHKOWSKI'S RULE:

Energy layers are defined by the principal quantum number, n.
The lowest-energy layer corresponds to n = 1. This is the layer in which the electrons are linked the strongest to the nucleus.

The layer defined by n = 1 can hold maximum **2 electrons**.
The layer defined by n = 2 can hold maximum **8 electrons**.
The layer defined by n = 3 can hold maximum **18 electrons**.
The layers defined by n >3 can hold maximum **32 electrons**.

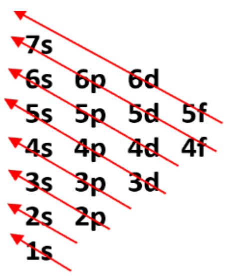
Each of the energy layers is made of several **sublayers.**
These sublayers are defined by letters: s, p, d, f.

Sublayer s can hold maximum **2 electrons**.
Sublayer p can hold maximum **6 electrons**.
Sublayer d can hold maximum **10 electrons**.
Sublayer f can hold maximum **14 electrons**.

Layer n = 1 is made of only 1 sublayer: 1s
Layer n = 2 is made of 2 sublayers: 2s 2p
Layer n = 3 is made of 3 sublayers: 3s 3p 3d
Layers n = 4 and n = 5 are made of 4 sublayers: 4s 4p 4d 4f and 5s 5p 5d 5f
Layer n = 6 is made of 3 sublayers: 6s 6p 6d
Layer n = 7 is made of 1 sublayer: 7s

The Z electrons are distributed around the nucleus in ascending order of energy, starting with the lowest-energy sublayer.

They progressively fill the layers and sublayers in the order indicated by the arrows (diagonals).



Notation:
$1s^2 2s^2 2p^6 3s^2$… until all Z electrons are positioned.

A layer is said to be **saturated** if it contains the maximum number of electrons it can accommodate.
The **outer** layer (or **valence** layer) is the last layer to be filled.
A layer is said to be **internal** when it is not the last layer filled.

Ex : Electron configuration (or structure) of sodium Na (Z = 11) : Na $1s^2\ 2s^2\ 2p^6\ 3s^1$
Following the example of sodium, give the electron configuration of the following atoms: O (Z = 8), Ne (Z = 10), Si (Z = 14), Ar (Z = 18), Pu (Z = 94).

HL Note: Ionization energies and electron configuration.

The electron configuration of an atom can be deduced experimentally from the measurement of the successive ionization energies.

Ex: For Magnesium (Ionization energies given in kJ.mol^{-1})

IE_1	$Mg \longrightarrow Mg^{+}$	737.7	
IE_2	$Mg^{+} \longrightarrow Mg^{2+}$	1450.7	+96%
IE_3	$Mg^{2+} \longrightarrow Mg^{3+}$	7732.7	+433%
IE_4	$Mg^{3+} \longrightarrow Mg^{4+}$	10542.5	+36%
IE_5	$Mg^{4+} \longrightarrow Mg^{5+}$	13630	+29%
IE_6	$Mg^{5+} \longrightarrow Mg^{6+}$	18020	+32%
IE_7	$Mg^{6+} \longrightarrow Mg^{7+}$	21711	+20%
IE_8	$Mg^{7+} \longrightarrow Mg^{8+}$	25661	+18%
IE_9	$Mg^{8+} \longrightarrow Mg^{9+}$	31653	+23%
IE_{10}	$Mg^{9+} \longrightarrow Mg^{10+}$	35458	+12%
IE_{11}	$Mg^{10+} \longrightarrow Mg^{11+}$	169988	+379%
IE_{12}	$Mg^{11+} \longrightarrow Mg^{12+}$	189368	+11%

The increase from IE_1 to IE_2 is “small”: The first 2 electrons are in the same layer.
The increase from IE_2 to IE_3 is “huge”: The 3rd electron is in a lower layer.
The successive increases from IE_3 to IE_{10} are “small”: 3rd to 10th electrons are all in the same layer.
The increase from IE_{10} to IE_{11} is “huge”, while the increase from IE_{11} to IE_{12} is small: 11th and 12th electron are in the same layer, with is lower than the previous one.
There is no IE_{13}, which means that a magnesium atom has only 12 electrons.

- ⇨ **The electron cloud of a magnesium atom has 3 layers. The first one has 2 electrons, the second one has 8 electrons and the valence layer has 2 electrons: $1s^2\ 2s^2 2p^6\ 3s^2$**