Atomes et molécules

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Chapter 2 : Evolution of atomic models

Introduction

Description of main steps of evolution of thoughts regarding the electronic structure of the atom …

… example of the way in which science evolves.

Introduction

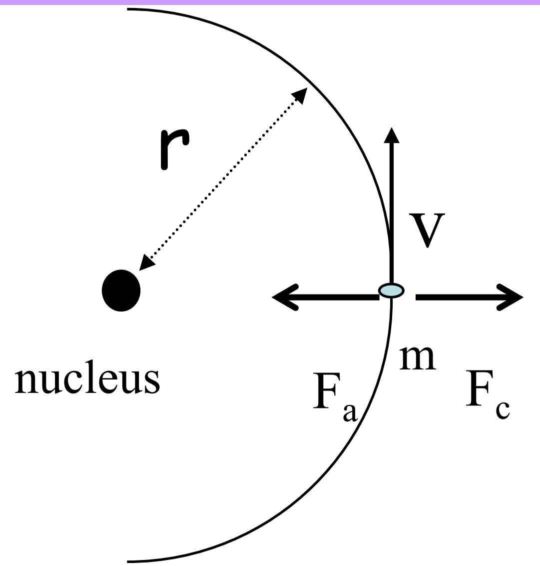
Gathering of **experimental** data available at a given moment in time (observations/measurements).

Proposing a **theory**.

Construction of **models** (= mathematical formalization of the problem) allowing to interpret the whole or part of the experimental data.

A new model is necessary when the facts derived from new experiments cannot be explained by the model currently accepted.

A new good model never substitutes an old one: it includes it, completes it and refines it.



Application of classical mechanics laws

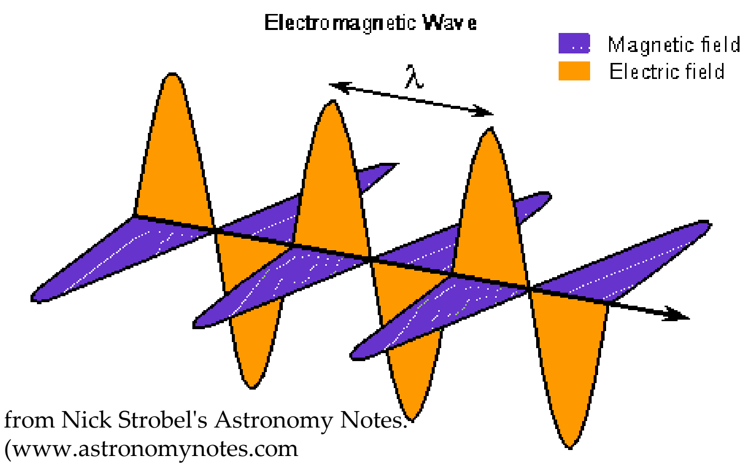
Calculation of electron total energy ($E_T = E_K + E_P$)

$$E_{total} = -\frac{1}{8\pi\varepsilon_0}\frac{e^2}{r} = \frac{constant}{r}$$

The electron energy is a continuous function of the distance electron – nucleus.
According to electromagnetic laws , the electron should radiate, loose energy and fall on the nucleus !!!
Another model is necessary

Wave nature of light

At the end of the 19th century James Maxwell defines light as an electromagnetic wave traveling at a constant speed in vacuum. This speed is c ~ 300000 km/s ($3x10^8$ $m.s^{-1}$.)



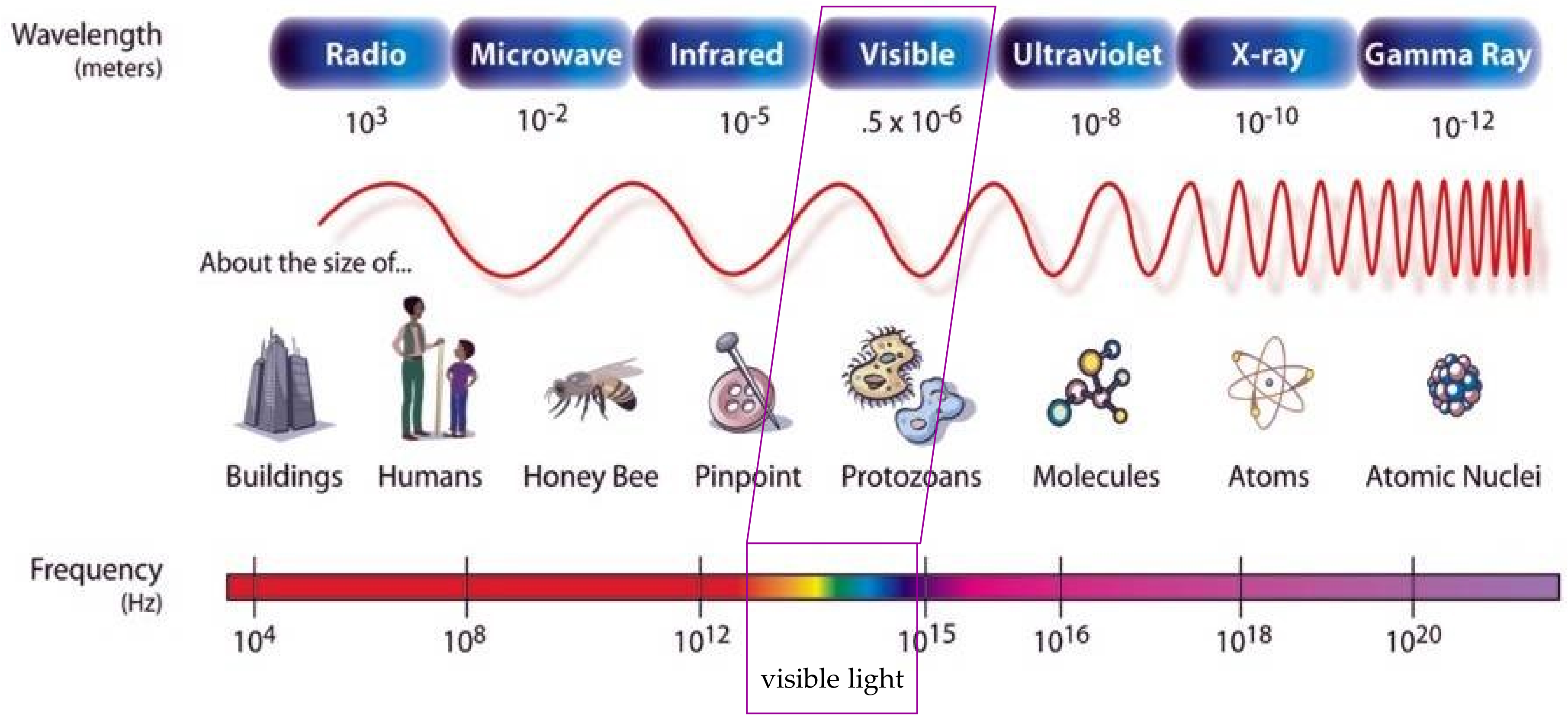
from Nick Strobel's Astronomy Notes.
(www.astronomynotes.com

He defines an electromagnetic wave as an oscillation of interrelated electric and magnetic fields

Light (and any other wave) is characterized by its frequency ν (number of oscillations per second of the light wave, measured in Hz) or by its wavelength λ (measured in m.)

$$\boxed{\lambda(m)\nu(s^{-1}) = c(m/s)}$$

Visible light is nothing more than a small window in all the possible electromagnetic waves (which also include gamma rays, X-rays, ultraviolet, infrared and radio waves)



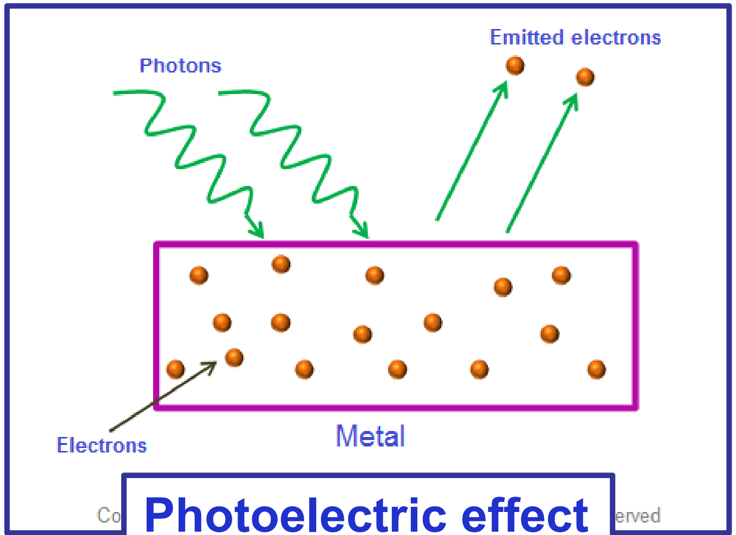
Corpuscular nature of light

1905 : Albert Einstein → suggest that luminous energy is someway ‘granular’ in nature.

This ‘grain of energy’ will be called photon in 1926. Then a new particle is born. This particle has no mass.

Energy of light:

$$E = h\nu = h\frac{c}{\lambda}$$



Photoelectric effect

c: speed of light in vacuum (m s^{-1}) =(3.10^{8} m.s^{-1}
h: Planck’s constant (Joule s) = 6,62 . 10^{-34} J.s
λ: wavelength of associated radiation (m)

1900: Max Planck → postulate the idea that energy exchange (absorption or emission) can be given only by an integer multiple of a minimal quantity of energy (quantum).

He wrote :

$$\Delta E = nh\nu$$

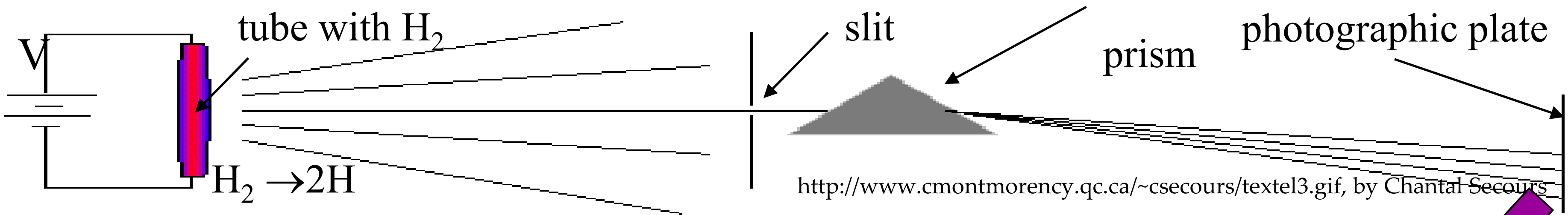
ΔE : variation in exchanged energy
ν : frequency of the emitted/absorbed radiation
h : Planck's constant (6.62×10^{-34} Joule.second)
n : an integer number

This means that the radiative energy is quantified, i.e., that it cannot be exchanged in any arbitrary amount.

1 - State of knowledge... - 1.4 Emission spectrum atomic hydrogen

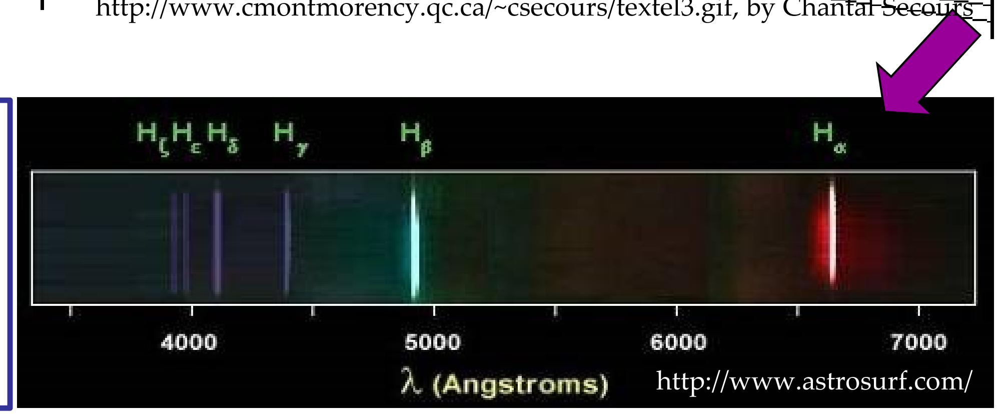
Experiments show that when gases are held at a small pressure in a sealed tube and subject to an appropriate electrical potential difference, they emit light.

Emission spectrum of atomic hydrogen



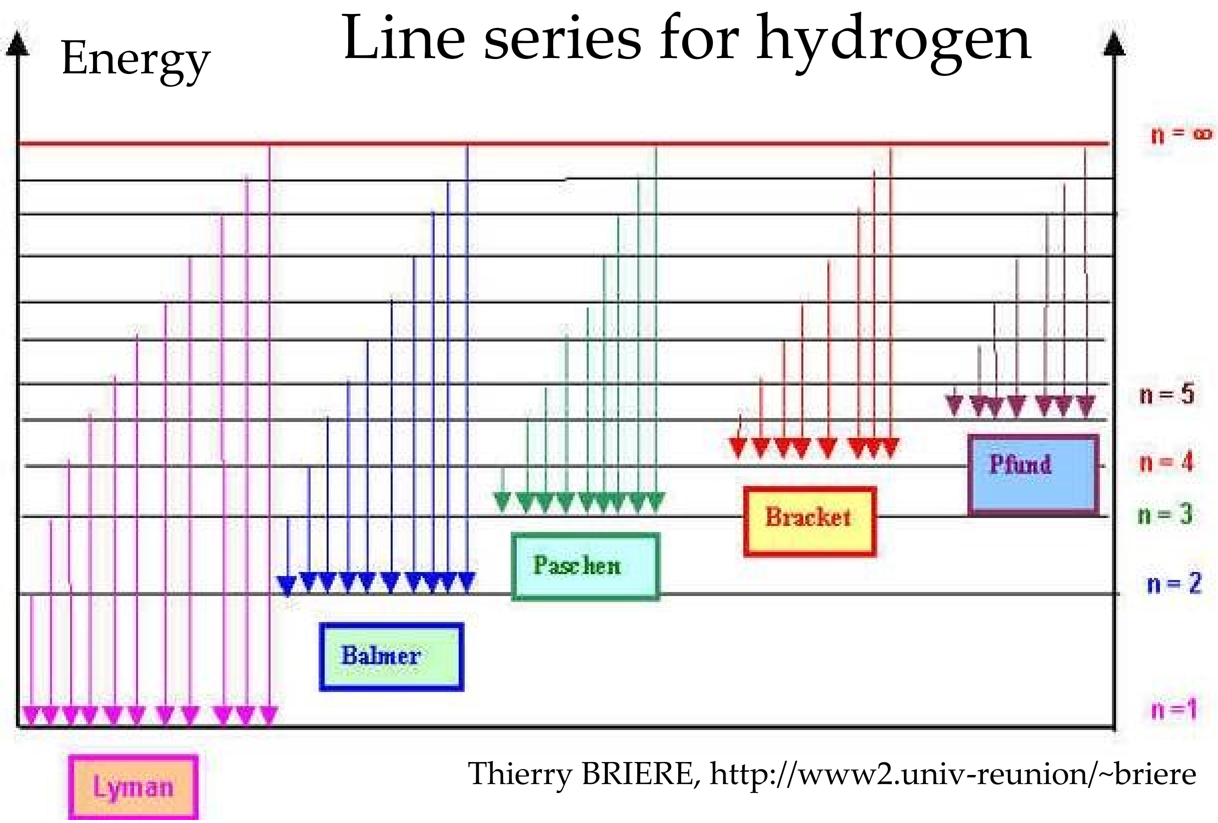
http://www.cmontmorency.qc.ca/~csecours/textel3.gif, by Chantal Secours

The spectrum of emitted light is composed of thin intense lines (line spectrum).
It is discrete: composed of a limited number of lines.



There are 4 lines in the visible domain. Their names: Hα, Hβ, Hγ and Hδ, occurring at 656, 486, 434 and 410 nm respectively.

1 - State of knowledge... - 1.4 Emission spectrum:atomic hydrogen



Thierry BRIERE, http://www2.univ-reunion/~briere

Studying the spectrum over a wide spectral domain (UltraViolet, Visible, Infrared) shows that the wavelength of the emitted radiation satisfies the Ritz relation:

An empirical general law wich describes the whole spectrum

$$\frac{1}{\lambda} = R_H\left(\frac{1}{p^2} - \frac{1}{q^2}\right)$$

p, q integers, p < q
RH: Rydberg constant = 109677,76 cm^{-1}

If p= 2 and q = 3 $\frac{1}{\lambda} = R_H\left(\frac{1}{3^2} - \frac{1}{2^2}\right) = 109677.76(1/4 - 1/9) = 15323$

1/15323 = 6.56 10^{-5} cm = 656 nm (Hα)

Contradiction with electromagnetic theory

From Rutherford we know that the e- orbit the nucleus with uniform speed, describing a circular orbit.

⇓

It moves in an electromagnetic field

From electromagnetism theory, the e- must emit radiation with an associated loss of energy. This would imply a slow down of the movement and a decrease in the radius of the movement.

⇓

The e- should 'fall' over the nucleus

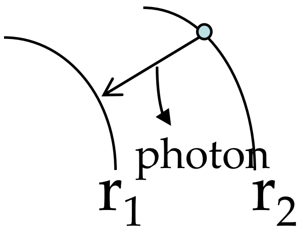
Experience shows that, in the fundamental state, the atom does not radiate:

It is stable and its half life seems to be infinite

Incoherence with the hydrogen emission spectrum

The excited H atom emits a radiation with energy E=hc/λ when an e- shifts from a level of energy to a lower one

$$\mathbf{E = hc/\lambda =} E_{\text{total(2)}} - E_{\text{total (1)}}$$



From Rutherford's model:

$$E_{total(1)} = -\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r_1} \quad \text{and} \quad E_{total(2)} = -\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r_2}$$

Therefore:

$$\frac{1}{\lambda} = -\frac{e^2}{4\pi\varepsilon_0 hc}\left(\frac{1}{r_2} - \frac{1}{r_1}\right)$$

As there is no constraint over the values of the radii, the atomic hydrogen spectrum should be continuous!!!

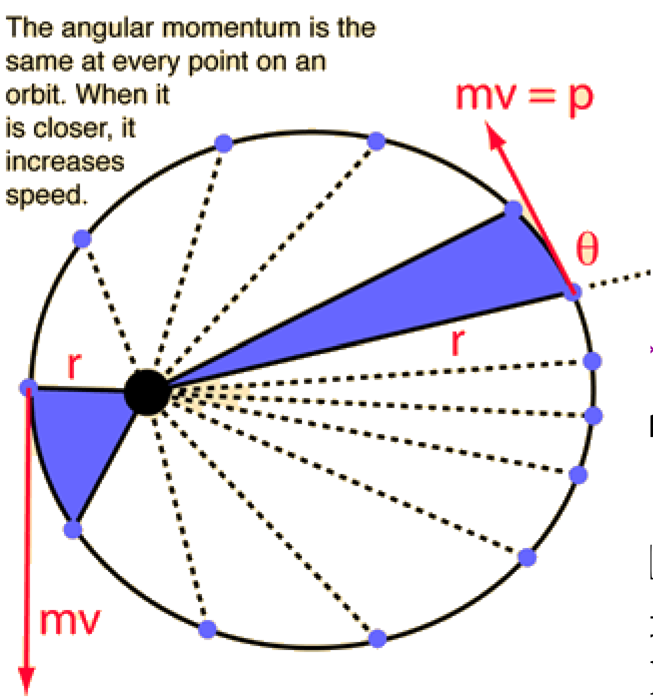
2 – Quantum model of the atom - 2.1 Bohr model (1913)

1913: Niels Bohr → proposes a model that avoids the 2 critics to the Rutherford model and presents the Bohr postulates:

* The electron moves in a circular orbit around the nucleus, under the coulombic influence of the later, following classical mechanics

* **Only certain electronic orbits are allowed: those for which the angular moment of the electron L is a multiple of h/2π**

QUANTIFICATION CONDITION : $L = mvr = nh/2\pi$



h: Planck constant (6.626×10^{-34} J.s) n: integer m: mass v: velocity

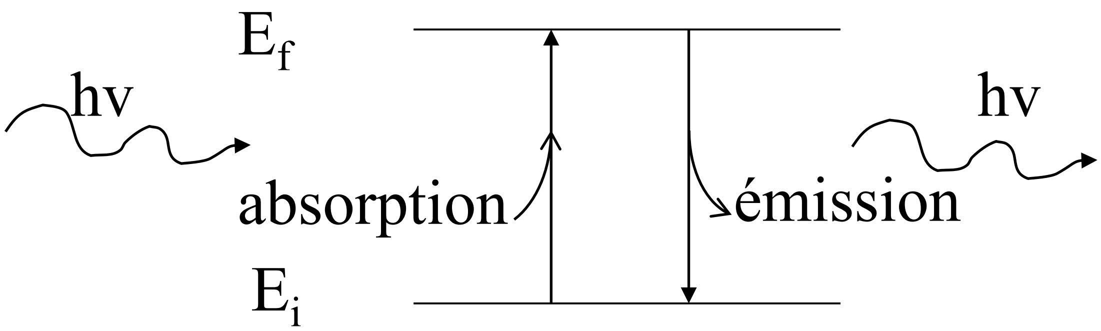
* In this allowed trajectory the electron does not emit radiation: it is on a stationary state (Etotal = constant)

Radiation is emitted/absorbed when an lectron moves discontinuously from a ate with energy Ei to one with energy Ef. he frequency of the radiation is:

$$\nu = \frac{E_f - E_i}{h}$$

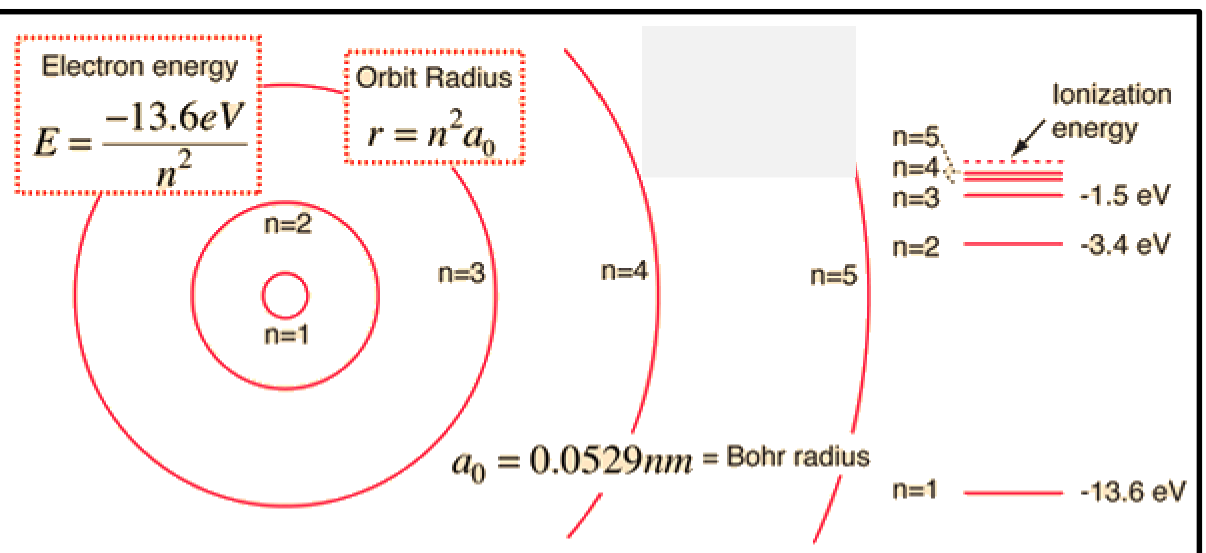
2 – Quantum model of the atom - 2.1 Bohr model (1913)

For the change of orbit to take place, the energy of the absorbed/emited photon has to be equal to the energy difference between the orbits



$$\boxed{E_f - E_i = h\nu}$$

In the absence of external excitations, the electron is found on the trajectory with the lowest energy: **fundamental state**.



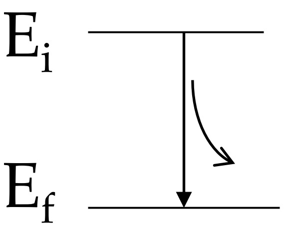
Orbit radius: $r = n^2 a_0$
$a_0 = 0.0529$ nm = Bohr radius

Bohr's model consequences

The total energy of the electron is quantified (depends on an integer value n):

$$\boxed{E_{total} = -\frac{me^4}{8\varepsilon_0^2 h^2}\frac{1}{n^2} = -\frac{cons\tan te}{n^2} = \frac{-13.6\,eV}{n^2}}$$

With this relation, Bohr explains the Ritz empirical relation:



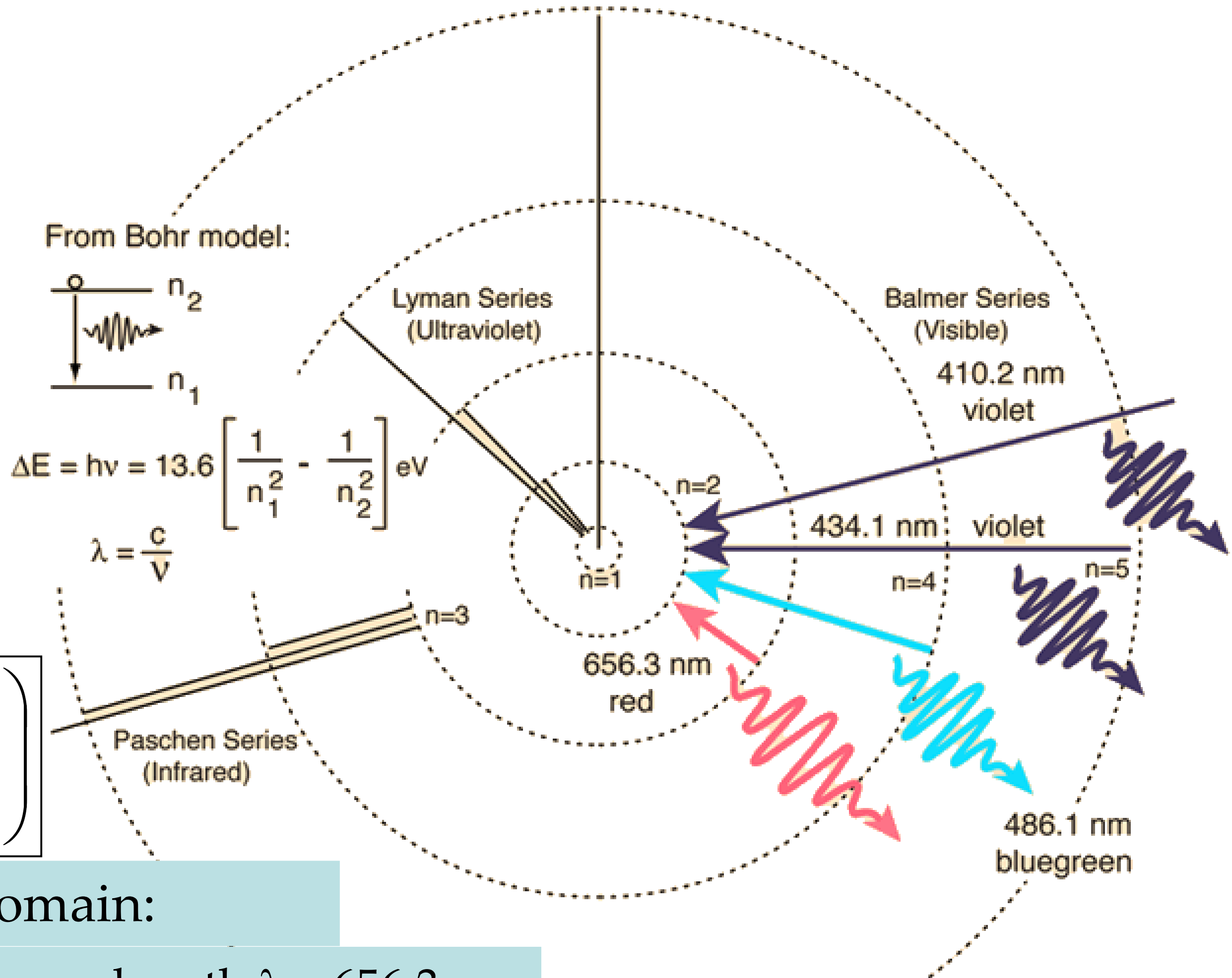
Émission $\Rightarrow$ $$E_i - E_f = \frac{hc}{\lambda} = -\frac{me^4}{8\varepsilon_0^2 h^2}\frac{1}{n_i^2} - \left(-\frac{me^4}{8\varepsilon_0^2 h^2}\frac{1}{n_f^2}\right)$$

$$\frac{1}{\lambda} = -\frac{me^4}{8\varepsilon_0^2 h^2}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

Which is the same as $$\frac{1}{\lambda} = R_H\left(\frac{1}{p^2} - \frac{1}{q^2}\right)$$ if $$R_H = -\frac{me^4}{8\varepsilon_0^2 h^2}, n_f = p, n_i = q$$

Calculating R_H from this expression, Bohr finds a value in excellent agreement with the experimental value.

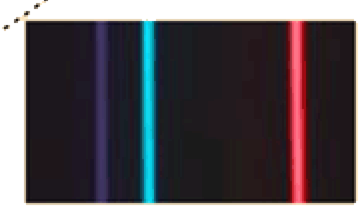
Bohr's model predicts the atomic hydrogen spectrum



$$\frac{1}{\lambda} = R_H\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

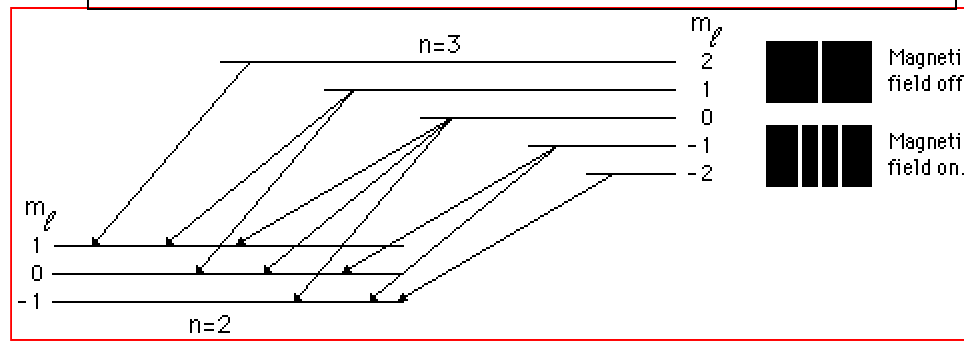
rays in visible domain:

$n_i = 3$ to $n_f = 2 : \Rightarrow$ wavelength $\lambda = 656.3$ nm
$n_i = 4$ to $n_f = 2 : \Rightarrow$ wavelength $\lambda = 486.1$ nm
$n_i = 5$ to $n_f = 2 : \Rightarrow$ wavelength $\lambda = 434.0$ nm
$n_i = 6$ to $n_f = 2 : \Rightarrow$ wavelength $\lambda = 410.2$ nm

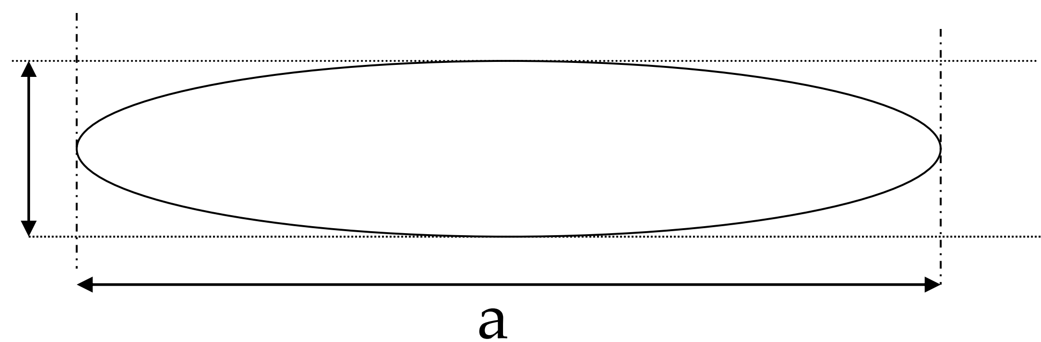


The Bohr model predicts the isolated atomic hydrogen spectrum, but fails to predict the spectrum of an hydrogen atom in an exterior magnetic field. In this case the observed lines subdivide into many others (Zeeman effect)

Effect of magnetic field on H spectrum



1915: Sommerfeld → Interprets these lines based on elliptic orbits. The energetic state of the electron in the atom is then characterized by **2 supplementary quantum numbers: ℓ and m**



n: principal quantum number defining the smaller axis of the ellipse (b)

ℓ : orbital quantum number defining the flattening factor of the ellipse (1-b/a)

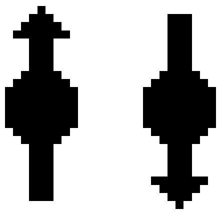
m: magnetic quantum number defining the ellipse orientation with respect to the electric or magnetic field.

Spin quantum number: s

Electron Intrinsic Angular Momentum
Experimental evidence like the hydrogen fine structure and the Stern-Gerlach experiment suggest that an electron has an intrinsic angular momentum, independent of its orbital angular momentum. These experiments suggest just two possible states for this angular momentum, and following the pattern of quantized angular momentum, this requires an angular momentum quantum number of 1/2.
With this evidence, we say that the electron has spin ½:

Electron spin: s = -1/2 or s= +1/2

Spin "up" and "down"



Introduction of 4 quantum numbers

Following the Bohr-Sommerfeld model the state of an electron in an atom is defined by 4 quantum numbers: **n, ℓ, m and s**.

The values of these 4 numbers 'identify' an electron in an atom (as a citizen can be identified by an address: city, street, number, floor)

This result will not be contradicted nor modified by the wave model (that we will see next) which contributed to a new concept concerning the electronic organization of atoms.

Principal quantum number: n

n can take all integer positive values.
n = 1,2,3,… inf

n is the only quantum number that influences the energy of an electron in a hydrogen atom (Energy depends only on **n**)

$$\boxed{E_{total} = \frac{-13.6\ eV}{n^2}}$$

n defines a ‘shell’ of electrons.

A capital letter is assigned to each **shell** corresponding to a value of **n**:

n	1	2	3	4	5	6	…
shell	K	L	M	N	O	P	…

Secondary (orbital) quantum number: ℓ

> ℓ can take all integer values between 0 and **n**-1.
>
> ℓ = 0, 1, 2, 3,…**n**-2, **n**-1. Example: If **n** = 2, ℓ = 0 or 1

ℓ defines a sub-shell of electrons

A lowercase letter is assigned to each sub-shell corresponding to a value of ℓ

ℓ	0	1	2	3	4	5	…
name	s	p	d	f	g	h	…

Each sub-shell is named by a symbol composed of:

_ a number, the corresponding value of **n**

_ a letter, the corresponding value of ℓ

Exemple: sub-shell **1s** (**n** = 1 et ℓ = 0) , sub-shell **3d** (**n** = 3 et ℓ = 2)

Note: The electrons occupying these shells have the same name.

E.g.: electrons **1s**, electrons **3d.**

Magnetic quantum number: m

m *can take* (**2*ℓ + 1**) *integer values between* **- ℓ *and* + ℓ**

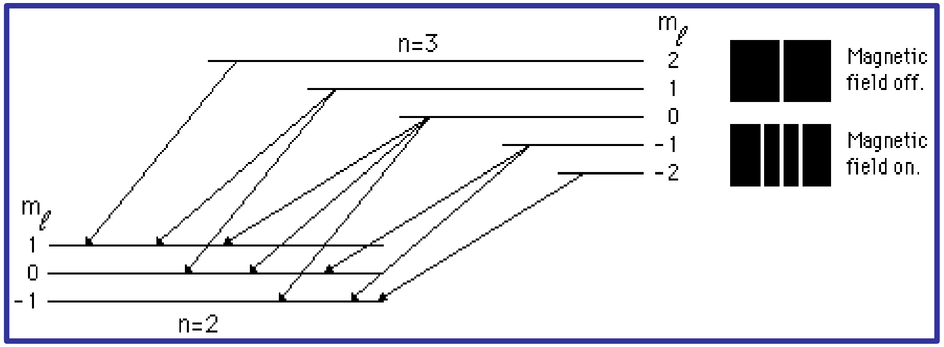
$$m = -\ell, -\ell+1, \ldots, -1, 0, 1, \ldots, \ell-1, \ell$$

m characterizes the energy sub-levels in a sub-shell of electrons

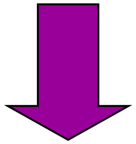
When an external magnetic field is applied, lines like the (n=3 → n=2) transition of hydrogen split into multiple closely spaced lines. This is due to the separation of the n=3 and n=2 energy levels according to the number of *m* possible *values.*

For n= 3, *ℓ* maximum = 2, m = -2,-1,0,1,2

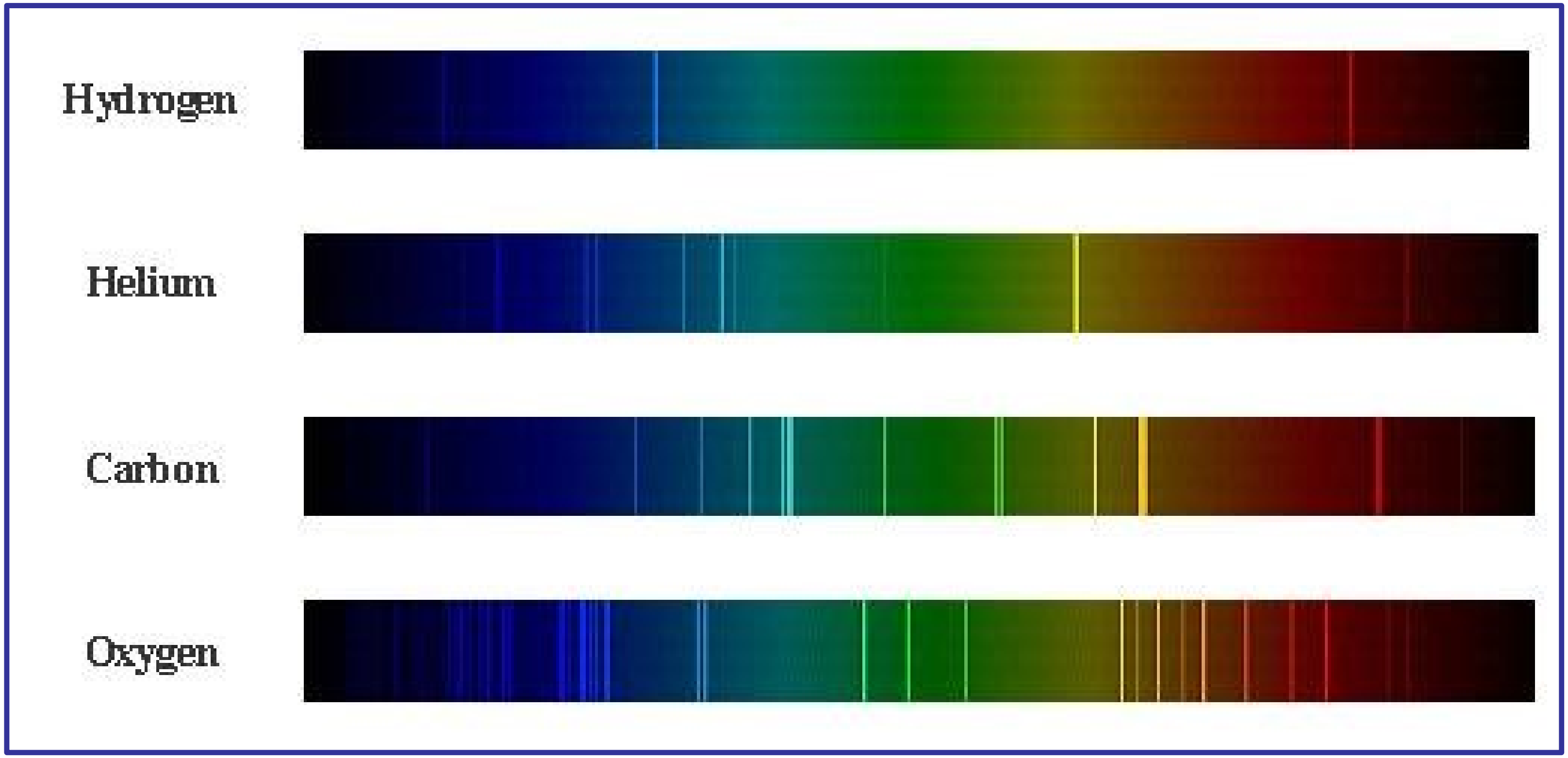
For n= 2, *ℓ* maximum = 1, m = -1,0,1



Multi-electron atoms: the Bohr-Sommerfeld theory cannot explain the multi-electron atoms spectra, starting from the Helium spectra.



It will lead to and be replaced by a new model provided by wave mechanics.



Wave-particle duality

Light shows properties that can be interpreted as waves (continuous phenomenon) and at the same time as a set of particles (discrete phenomenon).

A monochromatic light ray that propagates as a wave $\Rightarrow$ characterized by its wavelength λ

can be described from a particle point of view $\Rightarrow$ by photons of energy $E = h\dfrac{c}{\lambda}$

1924: Louis de Broglie → generalizes this idea of duality, suggesting that every material particle (also the electrons) can be considered to have wave and particle properties.

He relates the two descriptions by the relation:

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$

λ : wavelength
p: linear momentum

wave description

wave quantum mechanics

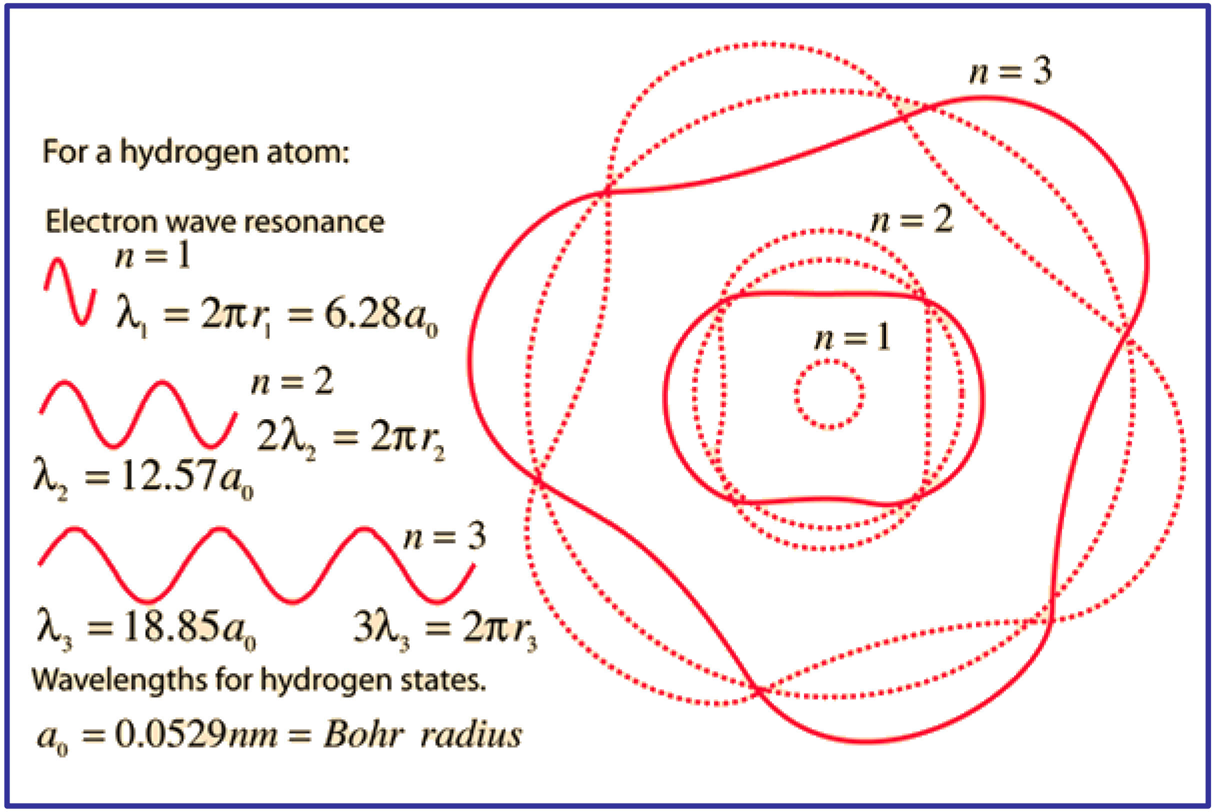
Particle description

Classical mechanics

Every particle with linear momentum p is associated to a wave of wavelength λ

Looking back to Bohr's condition on the angular momentum : $L = mvr = nh/2\pi$ we can use $\lambda = h/mv$ and we find $2\pi r = n\lambda$.
The circumference of the electron orbit is a multiple of the electron wavelength.
This is the stationary wave condition, a resonance phenomenon.

Wavelength for different states of the hydrogen atom:



Heisenberg inequality (or uncertainty principle)

1927: Werner Heisenberg → The momentum and position of a particle cannot be known simultaneously

$$\Delta x \Delta p > \frac{h}{2\pi}$$

Δx: position uncertainty
Δp: momentum uncertainty

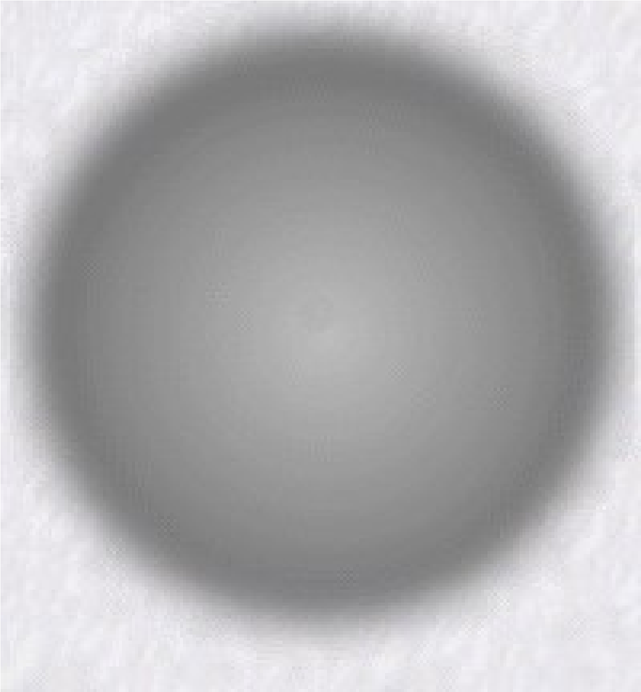
Applied to the electron this means we cannot know exactly where it is. We can only give the probability that it is at a certain point in space around the nucleus. The velocity is never zero!

The idea of quantized electron energy is **conserved** (the energy can only take certain values, defining the energy levels among which the electrons are distributed)

BUT!

The idea of stable and geometrically well defined orbits for the electrons:
_ circular (Bohr)
_ elliptical (Bohr-Sommerfeld)
is **abandoned**:

it is replaced by the concept of **probability of presence.**



The atom in wave mechanics

In wave mechanics the e- is not described as a point mass with an associated trajectory, it is considered as a **wave**.

Therefore, the electron doesn´t follow the laws of classical mechanics (like in the Bohr model). It follows **wave mechanics** laws.

The electromagnetic wave associated to the electron is a stationary wave. Its amplitude at each point in space is time independent. The amplitude is given by a mathematical function

the wave function, **Ψ (x,y,z)**

$\Psi(x,y,z)$ can be positive, negative, complex
Ψ has no physical meaning

BUT!

Ψ^2 : probability density of finding the electron in a particular position in space.

$\Downarrow$

The probability dP of finding the electron in an infinitesimal volume dV centered at some point in space (x,y,z) is given by:

$$\mathbf{dP = | \Psi^2 | \, dV}$$

There is a normalization condition: the probability of finding the electron somewhere in space should be one:

$$\int_{\text{space}} \Psi^2 \, dV = 1$$

QCM 6

L'absorption d'un photon de fréquence convenable par l'atome d'hydrogène ($Z = 1$) peut entraîner :

A. Un déplacement de l'électron vers un niveau d'énergie supérieure.

B. L'ionisation de l'atome d'hydrogène.

C. Aucune modification.

D. Un déplacement de l'électron vers une trajectoire plus proche du noyau.

E. La formation d'un isotope de l'hydrogène (le tritium caractérisé par $Z = 1$, $A = 3$, $N = 2$).

QCM 7

Lorsqu'un électron revient d'un niveau excité au niveau fondamental, il y a :

A. Emission d'une radiation électromagnétique **B.** Absorption d'une radiation électromagnétique

QCM 10

Parmi les propositions suivantes quelle(s) est (sont) celle(s) qui est (sont) exacte(s) concernant le "grain d'énergie" appelé photon en 1926 par A. Einstein :

A. Il s'agit d'une particule chargée positivement.

B. Il s'agit d'une particule chargée négativement.

C. Il peut transférer son énergie à de la matière.

D. L'énergie E d'un photon est définie par la relation $E = h\nu = hc/\lambda$, ν définissant la fréquence et λ la longueur d'onde du rayonnement qui lui est associé, h étant la constante de Planck et c la vitesse de la lumière dans le vide.

E. Aucune des propositions précédentes (de A à D) n'est exacte.

QCM 1

L'expression littérale générale des valeurs d'énergie permises pour l'électron de l'atome d'hydrogène dans le modèle de Bohr est du type :

☐ $E_n = +\dfrac{A}{n^2}$ ☐ $E_n = +\dfrac{A}{2n}$ ☐ $E_n = -\dfrac{A}{n^2}$ ☐ $E_n = +\dfrac{A}{n}$ ☐ $E_n = -\dfrac{A}{n}$

On rappelle que A est une constante et n est le nombre quantique principal

QCM 2

Parmi les propositions concernant les nombres quantiques n (principal), l (secondaire) et m (magnétique), laquelle(lesquelles) est(sont) exacte(s) ?

- ☐ l est toujours inférieur ou égal à n.
- ☐ m peut prendre $(2n + 1)$ valeurs entières.
- ☐ Dans un atome, toutes les sous-couches s ont la même valeur de l.
- ☐ Un couple (n, l) donné définit une case quantique.
- ☐ Le couple $(n = 2,\ l = 1)$ définit une case quantique $2p$.