QUANTUM MECHANICS

"Matter and radiation"

Foreword

Starting with Newton (17th century) the Physics and the Chemistry developed under a classical framework. This continued till the end of the 19th century. The common poin of all the theories was the determinism and the predictions based essentially on our perception of the surrounding reality. At the end of the 19th century the humans considered that they understood the essential of the nature and everything could be explained within the existing theoretical framework.

However, some twighlight zones begun to appear. And some scientists such as Max Planck, Niels Bohr and Albert Einstein started to consider that beyond the twighlight zone of the existing theories should be something else, more complex and sophisticated, beyond the explanation horizon provided by the so far developed theories.

Some observed phisical phenomena, unable to be explained by the classical theories constituted the starting point of a new theory in physics. This new theory radically changed the human deterministic approach over the surrounding universe at both microscopic and macroscopic scale.

These revolutionary concepts have been gradually developed, beginning with the early 20th century. A complete formalism has been rulled out around 1930. (see: "Thirty years that shocked Physics: The Story of quantum Physics" by George Gamow).

Then, more and more complex mathematical and physical formalisms, brought new shape and deeper insight on the quantum universe with amazing application potential in the developement of modern technologies and devices.

A serie of Nobel Prizes for Physics emerged for major discoveries within this new and fascinating research field.

We list below the major discoveries which led to the developement of the Quantum Mechanics:

1900 : Planck (Nobel 1918): black body radiation and energy quanta

1905: Einstein (Nobel 1921) : Photoelectric effect and energy quanta

1913 : Bohr (Nobel 1922) - Sommerfeld : angular momentum quantification

1916 : Millikan (Nobel 1923) - experimental proof for the Einstein's theory of photoelectric effect

1922: Stern & Gerlach : - experimental proof of angular momentum quantification. Spin angular angular momentum

1924: de Broglie (Nobel 1929) : particles behaving as waves (wave-particle duality)

1925 Davisson & Germer : - experimental proof of electrons behaving as waves

1926: Schrödinger (Nobel 1933) - wave equation for particles

Max Born (Nobel 1954): wave function and probability.

1927 : Uhlenbeck & Goudsmith : - spin hypothesis

Heisenberg (Nobel 1932) - principle of incertitude

1930 : Dirac (Nobel 1933), Pauli (Nobel 1945) - postulates of the new quantum mechanics, relativistic quantum mechanics.

① Limitations of the classical physics and hystorical hypotheses

Let's get into the mind of a scientists living at the end of the 19th century. They distinguished two distinct types of object:
→ matter and
→ radiation

The matter is constituted by localized particles defined at any instant of time by a position and a velocity. Their movement obey the classical mechanis laws.

The radiation (see Maxwell's theory) is defined by $\vec{E}$ and $\vec{B}$ in any point of space $\vec{r}$. These fields are described by the Maxwell's equations showing that light is an electromagnetic wave.

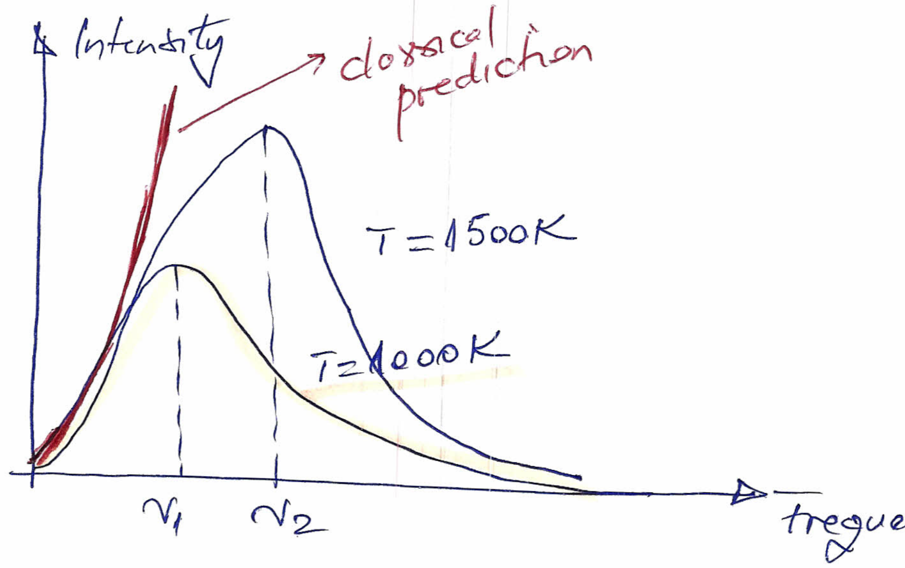
Maxwell's equations also correlate matter and radiation: e.g. electric charge is a source of electric field:

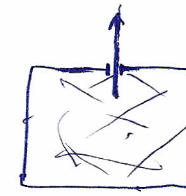
$$\oint \vec{E} \cdot d\vec{A} = \frac{Q}{\varepsilon_0}$$

The energy is therefore defined as a physical quantity that could vary continuously by changing the particle's velocity or the intensity of the electromagnetic field. Within this classical framework, some experiments gave results impossible to be explained.

a) Black body radiation

The experiment is based on the following observation: any body heated at a temperature T emits radiation. The experiment consist in heating a closed cavity with a small hole which allows the outward emission. The emitted radiation has, a priory, all frequencies (all λ). The result of the experiment is illustrated in figure below:





One experimentally observes that I increases with frequency, has a maximum and then decreases. The maximum is shifted for higher frequencies as the temperature increases.

The decrease of $I(\nu)$ measured experimentally is in disagreement with the classical predictions, and has been called <u>UV catastrophe.</u>

How the "classical" physics could explain the emission of radiation? We knew that the matter contains negatively charged electrons. The walls of the cavity are constituted by particles containing electrons. These particles vibrate at a certain temperature T $\Rightarrow$ accelerated movement. Following the classical theory of electromagnetism they will emit radiation (the walls are constituted by a large number of harmonical oscillators) which could emit radiation at all wavelengths. For the black body radiation at equilibrium (emission = absorption) the spectral density of energy within the cavity U_ν is equal to the number of vibration modes $g(\nu)$ possible per unit volume within $[\nu, \nu+d\nu]$ multiplied by the average energy of an oscillator that is k_BT.

The number of modes / unit volume can be calculated considering that inside the cavity only stationary waves can exist. The distance between these modes is:

$$\Delta k = \frac{2\pi}{L}$$

In 3 dimensions, the volume of a mode is: $(\Delta k)^3$. To count the number of modes one has to integrate in the space k_x, k_y, k_z and divide by the volume of a mode. (one multiplies by a factor 2, because we can have 2 light polarization - circular right / left)

$$g(k)dk = 2\frac{4\pi k^2 dk}{(2\pi/L)^3}\frac{1}{V} = g(\nu)d\nu$$

$k = \frac{\omega}{c} = \frac{2\pi\nu}{c}$

$V = L^3$

$$\Rightarrow \boxed{g(\nu) = \frac{8\pi\nu^2}{c^3}}$$

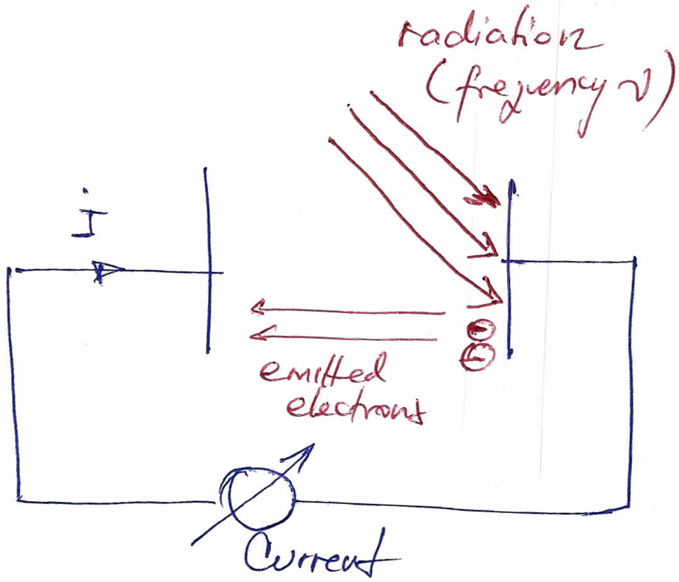
We get for the spectral density:

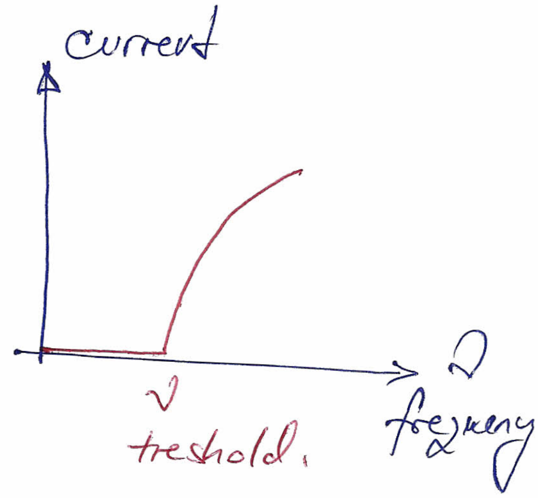
$$\boxed{u_\nu = \frac{8\pi\nu^2}{c^3} k_B T}$$

which describes well the black body radiation law at low frequencies but not at high frequencies.

b) The photoelectric effect

Another phenomenon has been observed: the photoelectric effect. From qualitative point of view there was no mistery in understanding the effect, but from quantitative point of view the situation was impossible to be explained. The experiment was the following: we send light (electromagnetic energy) on a metallic surface and, placing a collector under vacuum close to this surface, we can measure a current (figure):





Classically, one can understand that electrons can be detached from the metal by absorbing enough energy from radiations because the electric field of the electromagnetic wave can exert a force on electrons. Surprisingly, what people observed is that not the radiation intensity was the major factor but its frequency. Below a treshold ν no current has been detected, even for larger and larger intensities of the incident radiation.

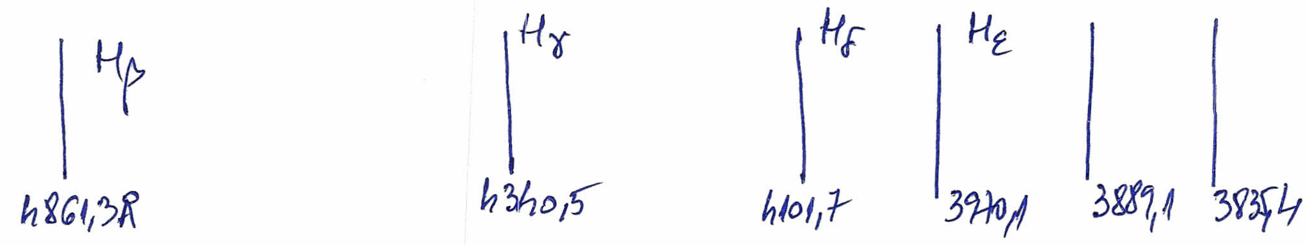
Moreover, for frequencies larger than the treshold one can measure the kinetic energy of the emitted electrons (apply a negative voltage to the collector and measure when $I \to 0 \Rightarrow E_c = \frac{mv^2}{2} = eV$). Classically we expect that E_c should increase when the intensity of the incident radiation is increased for a fixed frequency). This is not all all what happens: when increasing the intensity the number of emitted electrons increases but their kinetic energy remains constant!

c) Stability and emission spectra of atoms

At the end of 19th century the scientists used a model of atom which was able to explain a large number of experiments in physics and chemistry. This model was based on the existence of electron (discovered by J.J. Thomson in 1897) supposed to "gravitate" around the positivelly charged nucleus. (planetary model).

However, a huge problem arise when a charged particle moves (accelerated by centripetal acceleration) around a circular path: the electron should emit radiation, accordingly to the electromagnetic theory, so it should loose energy and fall on the nucleus!

Moreover, classically the electron could have a large number of possible orbites (grand number of possible solutions). This could qualitativelly explain the emission spectra of atoms supposing that when the electron passes from one orbit to another it emits radiation. An example of emission spectra for hidrogen is: (see cours Berkeley):



However, the emission of discrete spectra (precise frequencies / wavelengths for specific ellements), can not be explained within the classical approach.

(2) The hystorical hypotheses

a) Planck hypothisis of quantum action

Max Planck developed an exhaustive work for trying to explain the black-body radiation law: First, he found (grace to extremelly precise experiment developed by some other scientists) an exact formula which describes the experimental curve:

$$u_{\nu}(\nu) = \frac{8\pi\nu^2}{c^3} \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}$$

with $h = 6{,}626 \cdot 10^{-34}\ J \cdot s$

h = new physical constant (Planck constant).

We see that the average energy of an oscillator ~~kT~~ has been replaced by a more complex expression, unable to be justified within the classical theory.

Planck deduced this expression making a challenging hypothesis (1900): an harmonical oscillator cannot emit or absorb energy only in quanta (steps) proportional with frequency:

$$\Delta E = h\nu$$

and therefore, the energy levels of the oscillator should be: $E_n = n h\nu$.

A statistical calculation allows to show that the average energy of an oscillator is:

$$\langle E \rangle = \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}$$

So, Max Planck, put the first brick for a new theory allowing to describe the matter, defining a new constant h.

However, Planck only proposed a mathematical solution to an existing problem, he did not gave any "conceptual" explanation he has been looked for within the existing content of the classical physics agreed at his age.

b) Einstein : corpusculor concept of light

The first true valid concept of the new emerging quantum theory has been delivered by Albert Einstein in 1905 for explaining the photoelectric effect.

He proposes that the light can be only transmitted to the matter in pockets of $h\nu$ amplitude.

$$\boxed{E = h\nu = \hbar\omega = \frac{hc}{\lambda}}$$

$$\text{or} \quad E\,[eV] \cong \frac{1240}{\lambda\,[nm]}$$

$$1\,eV = 1{,}6 \cdot 10^{-19}\,C$$

This is equivallent of considering that a radiation of frequency ν is constituted by an assembly of particles having each the energy $h\nu$. This quantity has been later called energy quanta can be delivered to an electron of the metal to escape. This hypothesis allowed to explain the dependence on frequency for the photoelectric effect and allows writing an energy conservation law for the photoelectric effect.

$$h\nu = W + E_c$$

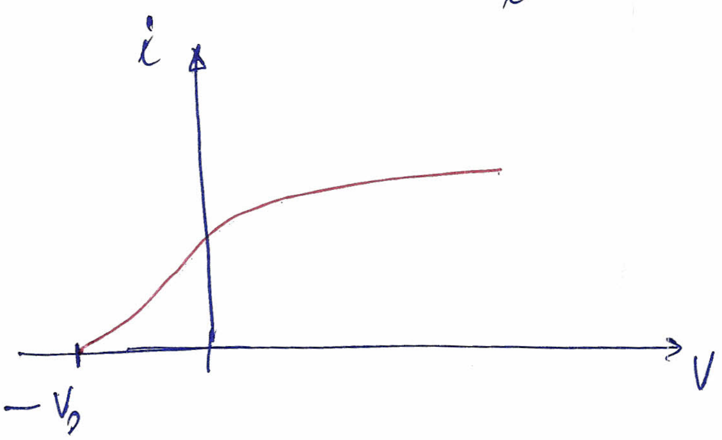
W = work function describing the minimum energy needed to remove an electron from the surface of a metal (material constant).

if $h\nu = W \Rightarrow E_c = 0$

for $h\nu < W$ no electron emitted $\Rightarrow$ $I = 0$

Stopping potential:

$$eV_0 = E_{c_{max}}$$



The quanta of energy are called PHOTONS.

The energy of an individual photon is

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

this applies for all regions of the electromagnetic spectrum.

Obs: Photons are not particles in the usual sense. They don't have rest mass and they can travel with the speed of light c (contrary to any other matter particle with $m \neq 0$ and $v < c$)

Moreover, photons have wave-aspects (frequency, wavelength) $\Rightarrow$ dual aspect (personality) of photons, as described later for other particles. (electrons, ...).

Photon picture explain other phenomena in which light is absorbed: Suntan: caused when light energy triggers a chemical reaction in the skin leading to a pigment increase (melanin)

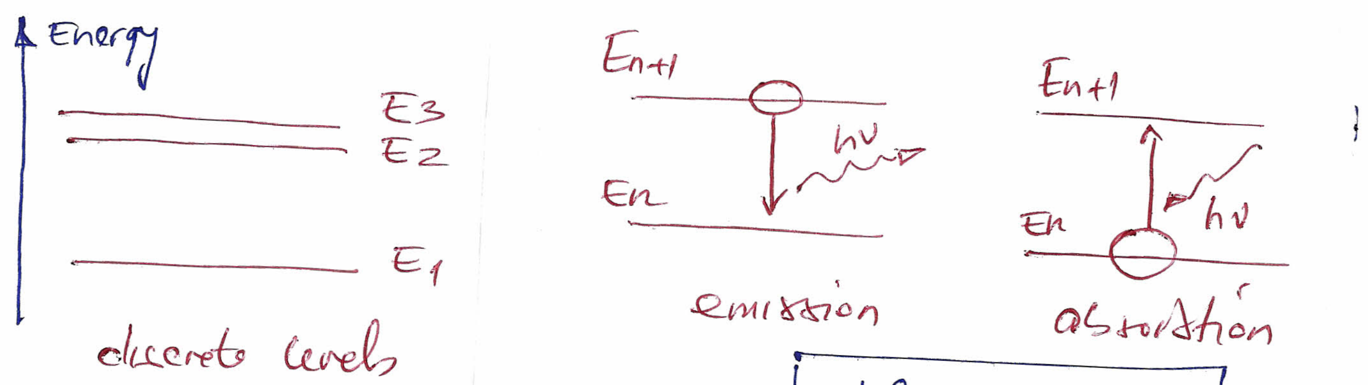
Photon momentum

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

c) Emission spectra of atoms: Bohr's model

To explain the emission spectra of the Hydrogen atom, Niels Bohr proposed in 1913 a model for the atom based on the planetary model, but combined with the concept of energy quanta.

He considers that the electron can move around the nucleus only on some orbits for which the angular momentum has a precise value. He proposes the quantification of orbital momentum as integer multiples of the Plank constant. This will subsequently lead to a quantification of the energy levels allowed for an electron in the atom. Then, Bohr postulates that when an electron passes from a level with higher energy to a level with lower energy, a photon will be emitted. Vice-versa, to get from a lower to a higher energy level, a photon has to be absorbed. Bohr enounced the following 3 postulates, he considered valid for any system at atomic scale (fig)



$$h\nu = E_{n+1} - E_n$$

(1) Energy quantification | A system at atomic scale can only exist in some stationary states. The energy of such system can only have discrete values defining the energy levels.

(2) Emission of photons | When the system passes from the stationary state of high energy E_n to a stationary state of lower energy E_m a photon will be emitted with the frequency

$$\nu_{mn} = \frac{E_n - E_m}{h}$$

(3) Absorption of photons | Vice-versa, the system can pass from a stationary state E_m to another stationary state E_n by absorbing a corresponding photon with the energy:

$$h\nu_{nm} = E_n - E_m$$

From the 1st hypothese, writing the fundamental principle of dynamics for an electron orbiting on a circular path of radius a_0 around the nucleus:

$$m|\vec{a}| = m\frac{v^2}{r_n} = eE = \frac{e^2}{4\pi\varepsilon_0 r_n^2}$$

and the quantification condition for angular momentum:

$$\vec{L} = \vec{r} \times m\vec{v} \quad ; \quad L = m v r_n = n\frac{h}{2\pi} = n\hbar$$

$\Rightarrow$ for the smaller radius orbit:

$$r_1 = a_0 = \frac{4\pi\varepsilon_0 \hbar^2}{me^2} = 0{,}529\,\text{Å} \quad \text{(Bohr radius)}$$

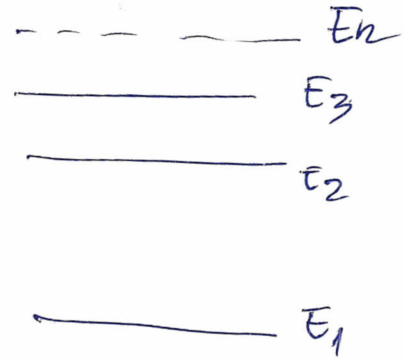
The energy levels will be:

$$E = E_c + E_p = \frac{1}{2}mv_n^2 - \frac{e^2}{4\pi\varepsilon_0 R_n}$$

$$\Rightarrow \boxed{E_n = -\frac{me^4}{8\varepsilon_0^2 h^2}\frac{1}{n^2} = -\frac{13{,}6}{n^2}\ (\text{eV})}$$

This formula is still valid for hydrogenoides atoms (with 1 electron on external shells):

$$\boxed{E_n = -\frac{Z me^4}{8\varepsilon_0^2 h^2}\frac{1}{n^2}}$$



This arangement of electronic levels allowed explaining the spectra of the Hydrogen.. The model fails to explain the spectra of more complex atoms, more complex quantum models have to be developed.

Hydrogen spectrum