-The first steps of quantum mechanics relate with the attempts for explication of
   a- Blackbody radiation behaviour
   b- The origin of photoelectric effect
   c- The origin of visible spectra emitted by hydrogen
In these attempts, the physicists introduced the same " restriction": _The quantity of transferred energy is expressed as a whole multiplier of a "basic quantity "._

Transferred energy = m* ε   **m = 0,+1,+2,………**   **(1)**
   "ε" a basic quantity of energy

Remember: In the classical physics, there is no such type of restriction. Every value of energy can be interchanged. We say that the **_energy_** is a **_continuous_** variable **_in classical_** physics and a **_discrete_** variable **_in quantum mechanics._**

BLACKBODY RADIATION

-When an object temperature overcomes a certain value it appears red dull. This means that it emits a visible radiation that appears red for us. A further temperature raising changes this colour to orange – yellow and then to white. The characteristics of this radiation depend on the object **_temperature_** and it is known as **thermal radiation**. Specific feature: **_Its apparent colour depends only on the temperature of "source" object no matter what is the material that constitutes it._**

- Based on the classical electrodynamics and thermodynamic, the physicists started the study of thermal radiation by the end of 19 century. At first, they _recorded the spectra_ and realised that its _energy is distributed in a large region of E.M. wavelengths_. The visible light is only one part of emitted energy (fig 1). The physicist developed a model that was based on **_a very big number of electric oscillating sources (called _oscillators_)._** **_Each oscillator is an SHO with frequency " f " and emits one E.M. wave with frequency " f " (corresponding wavelength λ = c/f)that is part of thermal radiation ._**
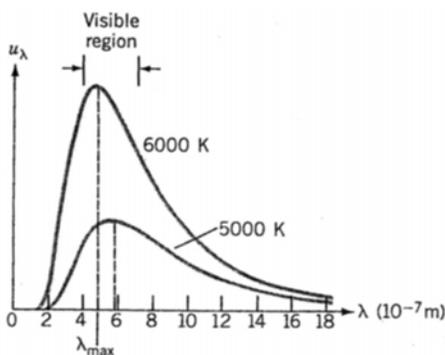
- The electric oscillating source describes the oscillation of electric charge of molecules in the material. These molecules move and oscillate with different speeds and frequencies that depend on the temperature. At a given temperature, there is a specific distribution of particles speeds and frequencies in the object. As far as the temperature is constant there is equilibrium and this distribution remains unchanged. To find this distribution, the
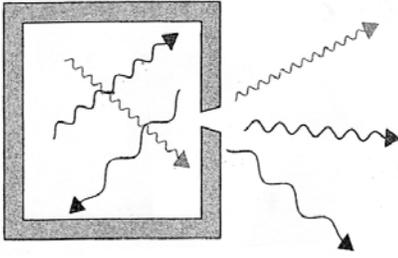
Fig 1

1

concept of the blackbody was used. **The black body is an ideal system that absorbs all radiations incident on it**. The best modelling for the blackbody is a closed cavity with only a tiny opening (fig. 2). A wavelet that enters the cavity has infinite low probability to get out anew and, at the end, is absorbed by cavity walls. The cavity walls are heated and then are

Fig 2

kept to a constant temperature value **T**. The cavity walls emit a radiation that has very low chances to get out of cavity. This radiation is absorbed by cavity walls after a number of reflections. So, after a short interval of time, the equilibrium is established in energy exchange between the walls and the radiation. After this moment, the energy density **u(T)**[J/m^3] of radiation and its distribution between different frequencies **u(T)$_\lambda$** remain constant. The radiation energy in interval λ, $\lambda+\Delta\lambda$ is **u$_\lambda$*$\Delta\lambda$** because

$$u_\lambda(T) = \frac{du(T)}{d\lambda} \qquad (2)$$

This *spectral energy density* **u(T)$_\lambda$** [J/m^4] is measured through spectral analysis (fig 1) of the very small radiation that can get out of the opening. So, we study the thermal radiation inside the cavity through this representative sample.

If **u(T)$_\lambda$** is know, the density of radiation energy inside the cavity is calculated as

$$u(T) = \int_{\lambda_{min}}^{\infty} u_\lambda(T)d\lambda \qquad (3)$$

Note that the expression (3) is equal to the surface under the graphs **u(T)$_\lambda$ = f(λ)** in fig 1.

-The results of multiple recordings on blackbody radiation spectra showed that:
 a) It is continuous (not a line spectrum)
 b) It does not depend on the material of cavity walls.
 c) It depends only on the temperature in cavity. When temperature is raised:
  c-1) the **energy density u(T)** increases.   c-2) the peak position shifts to shorter λ.

-The **Wien's first law** gives the relation between the *temperature* and *maximum position;*

$$\lambda_{max} * T = 2.898 * 10^{-3}[mK] \qquad (4)$$

wavelength measured in meters and temperature measured in degrees Kelvin(273+C^0)

The **Wien's second (radiation) law** gives an expression for **u(T)$_\lambda$ = f(λ)**

$$u_\lambda(T) = A * \lambda^{-5} e^{-B/\lambda T} \qquad \text{A, B two constants} \qquad (5)$$

The expression (5) produces good fitting with experimental results in the **near infrared spectrum** (*700-6000nm or 0.7- 6 μm*). The **Rayleigh- Jeans law** gives the expression

$$u_\lambda(T) = 8\pi k * T * \lambda^{-4} \qquad (6)$$

that fits well with recorded data for the far infrared region (>15μm).

-Max Planck considered the equilibrium between the walls and radiation in cavity from thermodynamic the point of view and applied the principle of maximum entropy. When trying to find an expression for the entropy through the total energy of oscillators (sources of radiation) at the cavity walls he got in front of two possibilities:

a) this energy can take any value (is continuous)- classical point of view
b) this energy takes only values that are multiples of an ***fixed minimum value*** "ε"

He used the second hypothesis to simplify the calculations without being conscious that this was the first step toward a new theory. Assuming that this ε value is

$$\varepsilon = h * f; \_ where \_ f = c / \lambda \tag{7}$$

he got the expression
$$u_\lambda(T) = \frac{8\pi hc\lambda^{-5}}{e^{hc/\lambda kT} - 1} \tag{8}$$

The **Planck's radiation law** (8) yields correctly the complete spectrum of thermal radiation if the value of *Planck' constant* is

$$h = 6.626 * 10^{-34} J * s \tag{9}$$

Note that expression (9) transforms to (5) for short λ and to (6) for long λ. (homework)

-While Planck introduced the quantization only as a mathematical artifice, Albert Einstein proved at 1906 that Planck law (expression 8) could be derived only if the energy of each oscillator is quantized by steps of "**h*f** ".

Einstein was the first who advanced clearly the quantum hypothesis as follows:

*The energy of an (molecular or atomic) oscillator can take only values that are integer multiples of "**h*f** "and the energy of oscillator in its nth "level" is*

$$E_n = nhf; \_\_ n = 1,2,3,4..... \tag{10}$$

Fig.3 Energy levels of a quantum oscillator
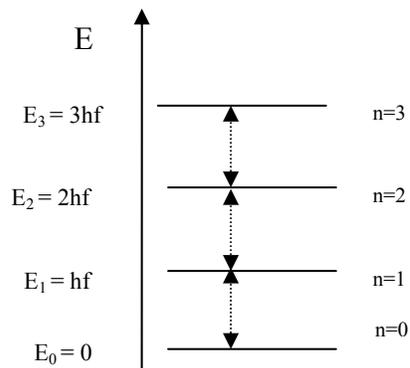
This hypothesis implies that one oscillator:

a) emits and absorbs only radiations which energy is a multiple of **h*f;**

b) the spacing between the energy levels depends on the oscillator frequency '**f** '.

3

THE PHOTOELECTRIC EFFECT

- By the end of 19th century J.J.Thomson showed that when the visible light illuminates an object done by alkali metals (Na, Ka, Cs), it becomes positively charged and this is due to the *electrons expelled* from it. ***The photoelectric effect is the emission of electrons by an object when a beam of light illuminates it***.

-The basic scheme used to measure the photoelectric effect is presented in figure 4. A beam of **monochromatic** light illuminates the plate P. The photoelectrons emitted from the plate P are attracted toward a metal cylinder C due to its positive electric potential V applied by a battery. The ejected electrons move in the electric circuit and their number
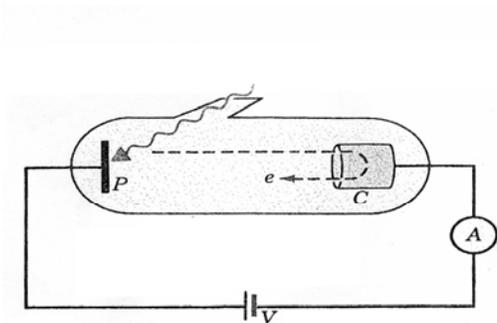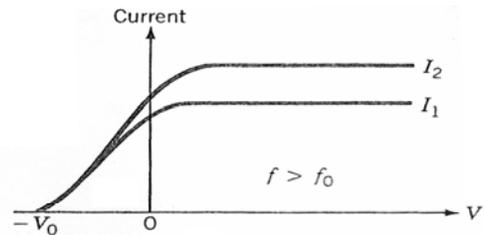

Fig 4

At positive accelerating potential differences, the maximum current is determined by the intensity of the radiation. However, the stopping potential does not change with the intensity.

Fig 5

is measured[1] by the ammeter A. The plate P and the cylinder C are enclosed inside a vacuum glass ampoule to avoid the collisions of photoelectrons with air molecules. The graphs in figure 5 presents the results of such an experiment. They show that:

1- When the potential of collector C is positive and bigger than a certain value V_{lim} the current in ammeter is constant. This result is explained as follows; the collector C absorbs all the electrons emitted from P (even those with the zero kinetic energy).
2- When the potential in collector C is lower than V_{lim}, a number of emitted electrons go out of plate P but cannot reach the collector C; the current in ammeter decreases.
3- When the polarity is reversed, the electrons are repelled from C and only the most energetic ones can reach the collector. When the negative potential in C reaches the value $-V_0$ the electrons with maximum kinetic energy ___can get till but not into___ C.

-The ***classical physics*** would:

a) use the *energy principle* to calculate the **maximum velocity** of emitted electrons

$$\frac{1}{2}mv_{max}^2 = eV_0 \qquad\qquad (11)$$

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[1] The current is proportional to the number of electric charges (electrons) passing the wire section in 1 sec..

Use the *wave model* of energy transfer from EM wave to electron which predicts:

b) emission of electrons *a certain time* after starting irradiation. This time is needed for
    the wave to transfer enough energy so that electron can get out of metal.
    In fact experiments show **instantaneous emission**.

c) Electron emission for any value of wavelength of incident radiation. The experiments
    show that there is a λ_{max} such that for $\lambda > \lambda_{max}$ no electrons are emitted.

d) Explain an **increase of current** with the **increase of light intensity** ($I_2 > I_1$). This fits to
    experimental records.

e) The existence of a *threshold intensity* value I_{thr} of light beam such that for $I_{light} < I_{thr}$
    no photoelectric effect happens. The measurements showed that :
    Provided that the light **wavelength $\lambda < \lambda_{max}$ (or frequency f > f$_{min}$) the** photoelectrons
    are emitted for *any light intensity* and **there is no** such **a I$_{th}$ value.**

-The points b,c,e showed a discrepancy of classical physics with measurement results.
  To resolve this situation, Einstein made a decisive hypothesis. He assumed that
    Radiation behaves as if it were composed of a collection of discrete energy quanta of
    magnitude each

$$E = h * f \tag{12}$$

h is the Planck constant and f the frequency of radiation

Note that these light particles are named as **photons** by G.H.Lewis in 1926.
-Then, Einstein developed the **quantum picture** for the photoelectric effect that follows;

a) *At one shot, a single photon gives up all its energy(and disappears) to a single*
    *electron and the electron is **ejected instantaneously** if the transferred energy is*
    bigger that the work function ϕ^2. The ejected electrons may have different values of
    kinetic energy depending on possible interactions inside the metal. Meanwhile,

b) *The **maximum of kinetic energy** available for the extracted electrons is found from*

$$h * f = \varphi + \frac{1}{2}mv^2_{max} \tag{13}$$

c) *This equation shows that there is a **threshold frequency f$_{min}$***

$$h * f_{min} = \phi \tag{14}$$

For $f \le f_{min}$ the electrons cannot leave the plate P because $K_{el} = h(f - f_{min}) = 0$

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[2] *the necessary minimum of energy to extract an electron from the surface of the material.*

d) As the energetic logic behind the equation (11) is right, one can calculate V_0 as

$$e * V_0 = h * (f - f_0) \qquad (15)$$

-The Einstein theory for photoelectric effect explains all features that appear in
 experimental measurements. Also, it offers a way to measure the work function ϕ
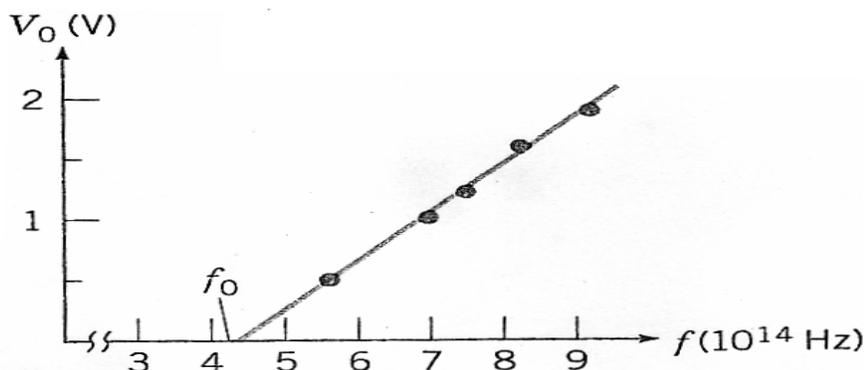 by the measurement of frequency f_0 (see graph in fig 5).

Fig 5

THE COMPTON EFFECT

- While Einstein used the concept for the first time in 1905 the name photon came from
  Lewis, in 1926. It was only after 20 years that this concept was widely accepted by the
  community of physicists. The reason was that the Maxwell theory explained perfectly
  the majority of radiations experiments and it seemed unreasonable to attack two of its
  foundations;
    a) the wave nature of light
    b) the continuous spectrum of radiation energy.

- In 1923, A.H.Compton advanced another decisive *experimental evidence on* the
photon. While studying the scattering of *X rays* by graphite crystals he recorded **two
bands;** One at **same** λ as the incident one (0.071nm) *and another one at $\lambda' > \lambda$* (fig 6)!!
The *classical* theory explains *only the first component*; "electrical charges oscillate with
the frequency of the incident radiation and reradiate at the same frequency".
Furthermore, Compton observed that *the **wavelength** of the second component **depends
on** the scattering **angle** but **not on the constituency** of the material in the target!!!*.

- Compton explained the presence of the second band by modelling X-rays as constituted
  by "**photons' particles**". He considered the collision of two particles (*photons - electrons*)
  and performed calculations in a **relativistic model of these particles**.
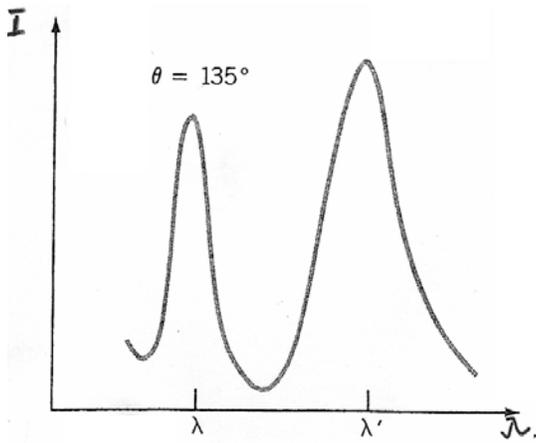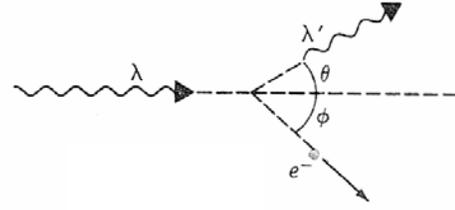
Fig 6

Fig 7

-The energy of X-ray photons is much larger than the **binding energy of external shells electrons** in atoms and molecules. So, during the interaction with X-ray photons, all the **loosely tied electrons** in the target can be **considered as "free electrons"**.

As the energy of a X-ray photon is $E = h*f$ and its *rest mass* is **zero**, one may find its **linear momentum** as

$$E^2 = p^2 c^2 + (m_0 c^2)^2 \rightarrow E = p*c \rightarrow p = E/c = \frac{h*f}{c} = \frac{h}{\lambda} \quad (15)$$

Considering the collision depicted in fig 7, for the **electron initially at rest** and the outgoing **photon deflected** along the **direction θ**, the energy conservation principle gives

$$(E_{el} + E_{ph})_{before\_coll} = (E_{el} + E_{ph})_{after\_coll} \rightarrow m_0^{el} c^2 + \frac{hc}{\lambda} = m_0^{el} c^2 + K^{el} + \frac{hc}{\lambda'} \quad (16)$$

By omitting the rest energy of electron on both sides and using $K^{el} = E - m_0^{el} c^2$ we get

$$\frac{hc}{\lambda} = \frac{hc}{\lambda'} + (\gamma - 1)*m_0^{el} c^2 \quad (16)$$

The conservation of **linear momentum** (see 15) for the two components yields

$$\sum p_x; \, \_\frac{h}{\lambda} = \frac{h}{\lambda'}\cos\theta + p\cos\varphi$$

$$\sum p_y; \, \_0 = \frac{h}{\lambda'}\sin\theta - p\sin\varphi \quad (17)$$

Note that $p = m^{el}*v^{el} = \gamma*m_0^{el} v^{el}$ is the electron momentum magnitude after collision. By combining the expressions (16-17) one may find the frequency shift

$$\lambda' - \lambda = \left(\frac{h}{m_0 c}\right)(1 - \cos\theta) \quad (18)$$

The quantity $(h/m_0 *c) = 0.00243\ nm$ is known as Compton wavelength.

Remember: *Maxwell theory (**classical physics**) considers that x-rays are E.M. waves and it **cannot explain** the presence of a λ'- component in scattered radiation. In the Quantum model X-ray are a beam of photons each containing the energy $E = hc/\lambda$ and linear momentum $p = h/\lambda$. This model explains the presence of a λ'- component in scattered radiation.*

THE LINE SPECTRA

- As seen in previous sections, a hot body emits a continuous spectrum of radiation. But, when recording the spectra of **rarefied gas** through which an electrical discharge passes (*or gas in very high temperature*), the scientists found <u>sharp lines</u>. Classical physics could not find any explanation for these spectra. These spectra became more important when the scientist realised that **<u>each chemical element has a set of characteristic lines</u>** that may be used to identify the element itself.

- The **visible spectrum** of hydrogen consists of four lines at **410.12**, **434.01**, **486.07** and **656.21** nm. The study of this spectrum started by empirical expressions that produce the measured experimental λ-values. The **Balmer formula** gives λ-values for H_2 lines

$$\lambda_m = 364.56 \frac{m^2}{m^2 - 4}; \rightarrow m = 3,4,5,6 \tag{19}$$

- The existence of line spectra required an explanation. The first satisfying explanation was given by Bohr model for the atom of hydrogen. When developing this model, Bohr included the idea of "**allowed orbits**" for electron revolution around the nucleus(fig 8). *This <u>unacceptable assumption for classical physics</u> produced a **quantified expression for the energy** and full explanation for the line spectra of hydrogen*. Bohr's results applie to all single electron systems such as **H**, **He+**, **Li++** provided that the nuclear charge of hydrogen (+e) is replaced by (+Ze). Bohr's expression for the energy levels of such systems is

$$E_n = -\frac{13.6 * Z^2}{n^2} eV; \_ n = 1,2,3...\infty \tag{20}$$

-The energy level diagram for hydrogen (**Z=1**) is shown if fig 9. Each **state** of the system (*electron orbit*) is defined by the **integer n** (called principal quantum number). When the atom is **unexcited**, the electron is in the **ground state (n =1)**. The energies of various levels are **E_1= - 13.6eV**, **E_2 = -13.6/2^2 = -3.4eV**, **E_3**=-13.6/3^2 = **-1.51eV** and so on. The **zero energy** of H- system corresponds to the **larger orbit** (n = ∞). So, the electron (*more precisely H-system*) has a **negative energy** for each **bound state**. In *normal condition*, the electron tents to be in the lower level of energy. When referring to a set of atoms, one says that, **in normal conditions**, majority of atoms *populate the lowest level of energy*.

-*The electron may be raised to a higher energy level by **absorbing one photon** only if the* **<u>photon energy is exactly equal</u>** *to the energy difference between two states of the nucleus-electron system*. If the photon energy is *larger* than 13.6eV (**ionization energy**) the electron is ejected out of the atom. Once in state with energy *n>1*, the atom may descent to an lower energy levels by **emitting** a photon.

- **Balmer's** series correspond to transitions *from higher levels to the level n =2*. These Photons constitute the four lines in visible spectrum of hydrogen we saw in the lab. The transitions from higher levels to level with n =1 and n=3 form respectively the *Lyman(all lines in UV)* and the *Paschen (all lines in IR)* series.
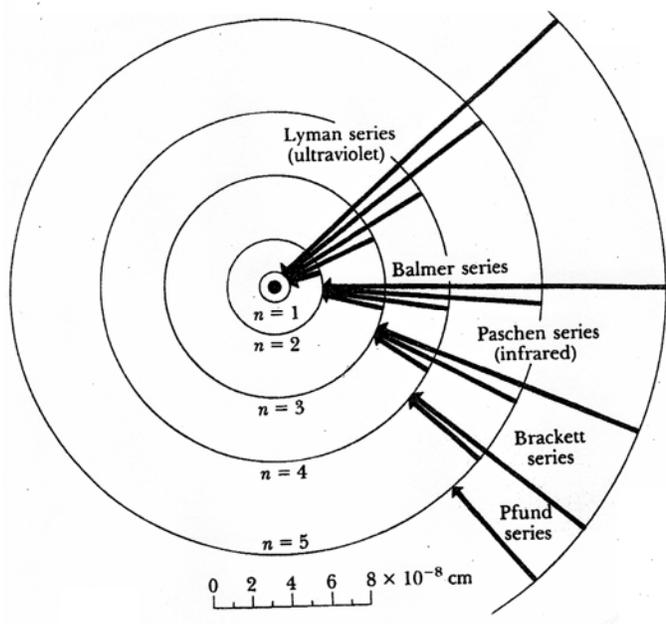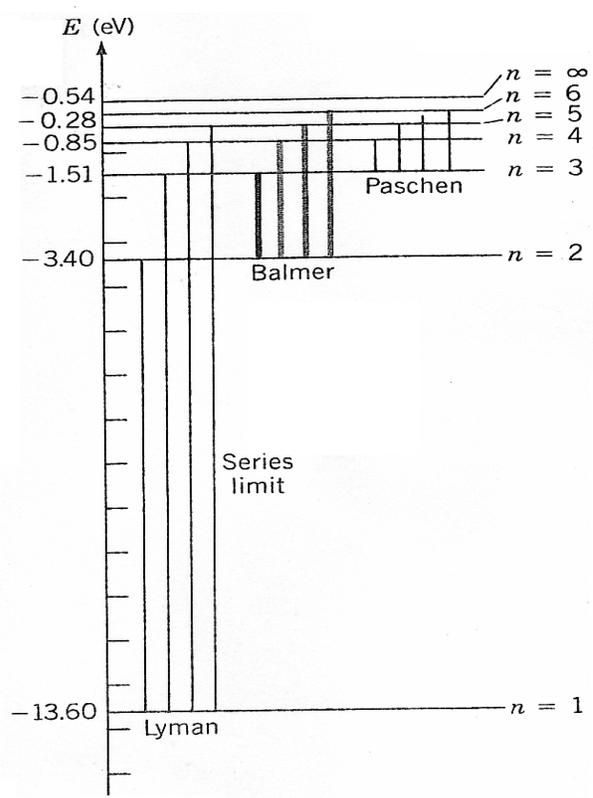

Fig 8

Fig.9 The energy level diagram for hydrogen. Light is emitted or absorbed when an electron makes a transition between two levels.