I Hystorical introduction to quantum mechanics

1. At the beginning of the 20th century, the development of classical physics was basically completed. There was an opinion that any physical phenomenon can be explained within the framework of existing physical theories. At least that's what physicists thought. Only two experiments needed explanation.

First one is a The Michelson–Morley experiment was performed between April and July 1887. Are compared the speed of light in perpendicular directions in order to detect the dependence of the speed of light on the speed of the light source. The result was steadily negative. Michelson–Morley type experiments have been repeated many times with steadily increasing sensitivity. The result of this experiment showed that the *ether* does not exist and the speed of light does not depend on the speed of the light source. This result cannot be explained within the framework of classical physics and led later to the **appearance** new theory - special relativity theory developed by Albert Einstein.

The second one is explanation of the radiation of absolutely black body.

2. The radiation of absolutely black body

We start from some basic definitions. Each body radiate, absorb and reflect electromagnetic waves.

Emissivity (radiational capacity) $r_{\omega,T}$ is the parameter characterizing the ability of the body to radiate electromagnetic weaves. If dW_e is the energy emitted from one square meter of the body per unit of time at temperature T in the frequency range [ω, ω + dω], then the emissivity of the body can be defined:

$$r_{\omega,T} = \frac{dW_e}{d\omega}$$

If dW_a is the energy absorbed and dW_f is energy **falling** on one square meter of the body per unit of time at temperature T in the frequency range [ω, ω + dω], then the **absorption capacity** of the body can be defined as:

$$a_{\omega,T} = \frac{dW_a}{dW_f}$$

The ability of the body to absorb energy is indicates which part of the energy that falls on the surface unit absorbs the body. As we can see right now, there is a special interest in the study of heat radiation of absolutely black body. An absolutely black body is a body where $a_{\omega,T} = 1$, which means that all the incident energy is absorbed by the body at all frequencies from 0 to infinity.

Based on general thermodynamic considerations (if the body is in thermodynamic equilibrium, this means that the radiated energy is equal to the absorbed energy), Gustav Kirchhoff has the following relationship between body radiance and absorption capacity: the ratio of radiation and absorption of all bodies is the same at certain frequency and temperature:

$$\frac{r_{\omega,T}}{a_{\omega,T}} = \epsilon_{\omega,T} \qquad \frac{r_1}{a_1} = \frac{r_2}{a_2} = \frac{r_3}{a_3} = \epsilon_{\omega,T}$$

where r_1 is the emissivity of the body 1 and the absorptive capacity of the same body a_1, the radiant capacity of the body 2 is r_2, and the absorbency of the same body a_2, and so on. Since the above-mentioned Kirchhoff law applies to all bodies, including the absolutely black body the universal function $\epsilon_{\omega,T}$, in the above-mentioned law, is equal to absolute black body radiant ability. In addition to the emissivity defined above, which characterizes the body's radiation at a given frequency, the integrated radiation capability can be reviewed too:

$$R_T = \int_0^{\infty} r_{\omega,T}\, d\omega$$

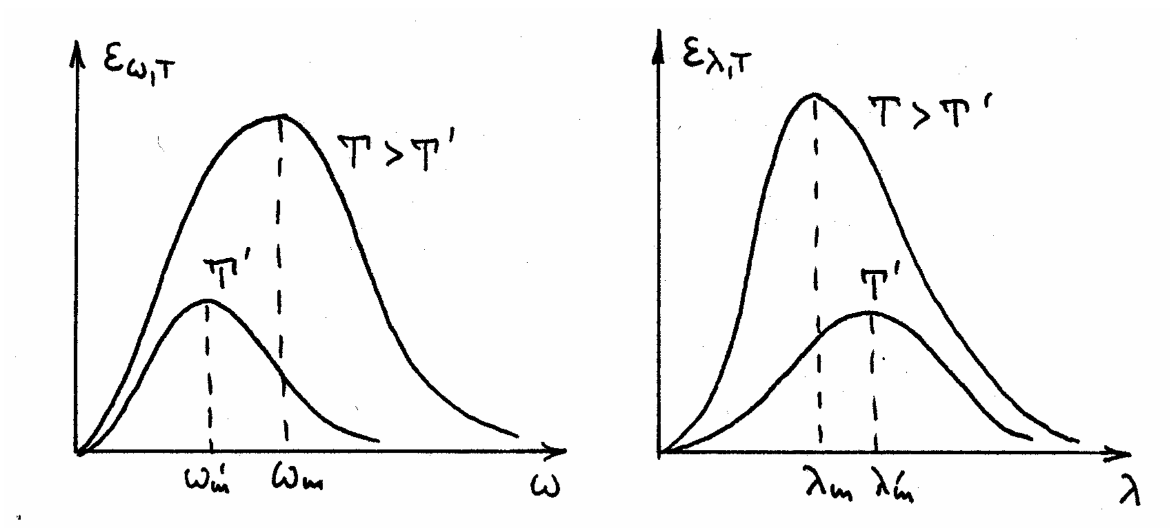
which characterizes the total radiated energy. J. Stefan and L. Boltzmann showed that the total radiated energy of an absolutely black body is proportional to the fourth degree of absolute temperature

$$R_T = \int_0^{\infty} r_{\omega,T}\, d\omega = \sigma \cdot T^4$$

the latter is called Stefan-Boltzmann's law. The Stefan-Boltzmann constant σ in the formula has a value in the SI system:

$$\sigma = 5{,}67 \cdot 10^{-8} \frac{W}{m^2 \cdot K^4}$$

As can be seen from the above, the study of thermal radiation actually comes down to studying the radiation of an absolute black body. If emissivity (universal function) for absolute black body is defined so we can define the emissivity for non absolutely black body by measurement of his absorption capacity. For absolutely black body this universal function is looks like so (this is a results of experimental measurements):



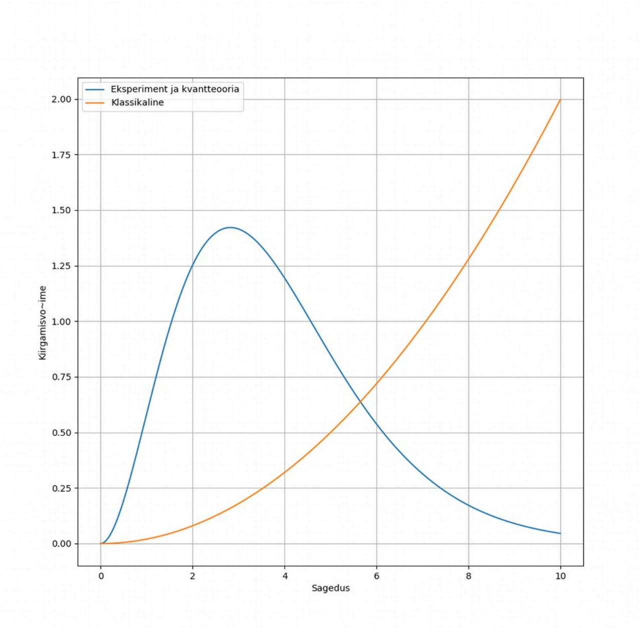
This function depend on temperature and have a maximum at frequency ω_m or wavelength λ_m .

Position of maximum can be defined by Wien's displacement law:

$$\lambda_m \cdot T = b,\ here\ b = 2{,}898 \cdot 10^{-3}\, m \cdot K$$

This equation can be used to estimate the surface temperature of the Sun. The maximum of spectral function (λ_m) for Sun is on the wavelength around 5000 A, this give us the temperature of Sun surface equal to 6000K. This value is not correct (must be around 8000 K) since the Sun is not a absolutely black body. But it is very close to it.

Here appearing a conflict with classical physics (we have a contradiction with classical theory of electromagnetic waves radiation). In classical physics, the emissivity function is proportional to the frequency squared. But in this case the integral radiation capability is infinite. This means that the body must radiate the whole heat energy very quickly and freezed to absolute zero temperature. For example, the human body temperature is equal to 310 degrees, is not a zero, as the classic physics predicts.



This paradox was solved in 1900.
Max Planck proposed the new hypothesis which can be used to solve this paradox. What happens if we suppose that the body radiate the electromagnetic energy discretely by a little portions with energy $E = n \cdot E_0 = n \cdot \hbar \cdot \omega, n = 0,1,2,\ldots$? Here $\hbar$ is universal constant (Planck constant). Planck showed that the emissivity function in this case is looks like so:

$$\epsilon_{\omega,T} = \frac{\omega^2}{4\pi^2 c^2} \frac{\hbar\omega}{e^{\frac{\hbar\omega}{kT}} - 1}$$

Here k – Boltzman constant , T – temperature of absolutely black body. The results of this investigation Planck sent to Einstein. He wrote that this is just an artificial hypothesis, and Einstein should not take it seriously (in spite of that equation give a correct function of emissivity, Stefan-Boltzmann law and Wien's displacement law). But despite of that Einstein further used this hypothesis to explain the very strange behavior of electrons in photo effect.

2. Photo effect

The photo effect consists in ejecting electrons from the metal surface under the influence of light. The photo effect was discovered in 1887 by H. Hertz, a man who experimentally proved the existence of electromagnetic waves. The basic regularities of the photo effect were determined by P. Lenard and J.J. Thomson in 1899. It wasn't much possible before, because electron was discovered only in 1897 by J.J. Thomson. The **basic regularities** of photo effect are:

1. The maximum speed of electrons depends on the frequency of the incident light, but does not depend on the intensity of the light.
2. Each substance has a red border of the photo effect, exist the maximum wavelength λ_m of light which does not produce a photo effect.
3. The number of electrons emitted from the metal surface is proportional to the light intensity.

This results could not be explained from the point of view of classical electrodynamics. But can be explained by applying the new Planck's quantum hypothesis. That did A. Einstein at 1905. He proposed that electrons can absorb electromagnetic waves by portions, quantum of energy, photons. Energy of one quantum is calculating so:

$$E_0 = \hbar \cdot \omega$$

Based on this, Einstein justified the photo effect with a simple energy conservation law: the energy of the photon **goes to** the electron exit work "A" and its kinetic energy can be calculated within a formula:

$$\hbar \cdot \omega = A + \frac{m \cdot v^2}{2}$$

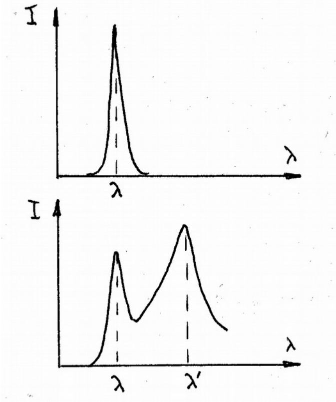
The first two regularities of the photo effect immediately follow directly from the above formula. The Einstein formula shows that the electron velocity depends only on the frequency of light but do not depend on intensity (the probability of two photons absorption is equal to zero for low intensity of light).

The second regularity stems from the fact that the photo effect can occur only when the photon frequency $\hbar \cdot \omega \geq A, \omega \geq \frac{A}{\hbar}$.

The last regularity can be explained by the fact that the number of electrons emitted depends on the number of absorbed photons (multiphoton absorption effects can be neglected due to a low probability).

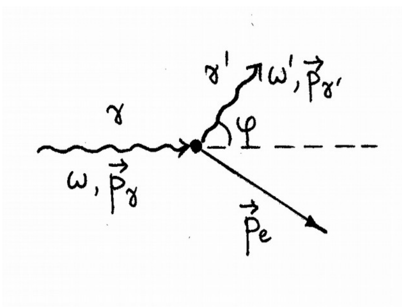
3. Compton effect

American physicist A.H.Compton in 1922 discovered the new effect for scattering of X-rays on free electrons (how the free electrons can be obtained? It is very simple, there is a lot of their in metals). On addition to the original X-ray with wavelength λ were founded the X-ray with large wavelength λ ' > λ. This effect got the Compton's name.

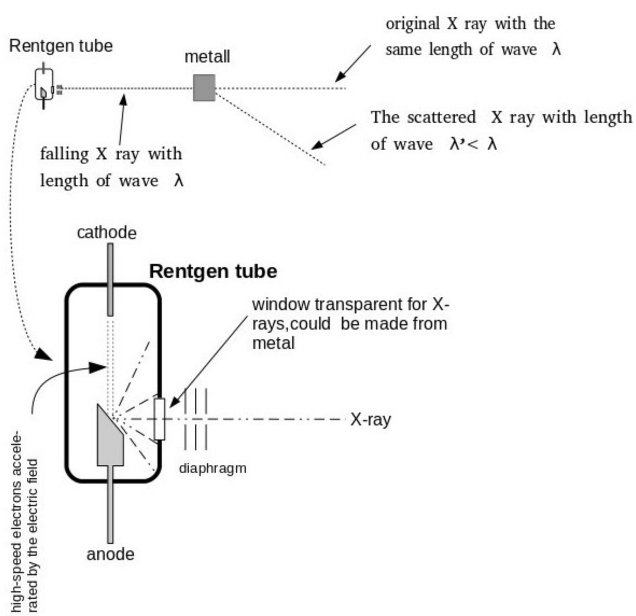


As you see on the figure we have two different spectrum components. The first with wavelength λ give the X-ray spreading in original direction (original X-ray). The second component (scattered X-ray) with wavelength λ' depends only on the angle of scattering.

The classical theory cannot explain the existence of second component. The electromagnetic wave is led to vibration of free electrons with the electromagnetic wave frequency (or wavelength). And these electron vibrations should not generate the electromagnetic waves with another frequencies (forced oscillations). But this effect have a simple and clear explanation if we present it as a scattering of photons on electrons. In this case we have two particles the first one is a photon moving from right side and has frequency ω and with momentum **p.** The second particle is a fixed electron. After scattering we have electron moving with momentum **p**$_e$ and photon with momentum **p'** and frequency **ω'**.



All that we need use to describe the Compton effect is a laws of momentum and energy conserving. But do not forget that photons and electrons are relativistic particles and we need to use relativistic mechanics to describe their motion.



<u>Appendix: photon and electron energy and momentum calculation.</u>
In this case we have to consider only kinetic energies (because particles are free).

<u>Calculation of kinetic energy:</u>
<u>For electrons:</u>

$E = m \cdot c^2$ (this is a most famous Einstein equation)-total energy including the rest energy and kinetic energy. We need **subtract** the rest energy from total energy to calculate only kinetic energy.

$$E=\frac{m_0}{\sqrt{\left(1-\frac{v^2}{c^2}\right)}}\cdot c^2=\sqrt{\left(p^2\cdot c^2+m_0^2\cdot c^4\right)};E_{kin}=m\cdot c^2-m_o\cdot c^2=m_0\cdot c^2\cdot(\gamma-1),\gamma=\frac{1}{\sqrt{\left(1-\frac{v^2}{c^2}\right)}}$$

For photons:

$$E=m\cdot c^2=\hbar\cdot\omega$$

Momentum:

For electrons:

$$\vec{p}_e=m_0\cdot\vec{v}\cdot\gamma$$

For photons:

$$\vec{p}=m\cdot\vec{c};m\cdot c^2=\hbar\cdot\omega;p=\frac{\hbar\cdot\omega}{c}$$

End of Appendix

The application of these formulas give us:

$\vec{p}=\vec{p}\,'+\vec{p}_e$ momentum conserve

$\hbar\cdot\omega+m_0\cdot c^2=\hbar\cdot\omega'+m\cdot c^2$ energy conserve

The shift of wavelength can be calculated directly. The square of first equation give:

$$p^2+p'^2-p\cdot p'\cdot\cos(\varphi)=p_e^2$$

after the substitution of momentum we get:

$(\hbar\,\omega)^2+(\hbar\,\omega')^2-2\hbar\,\omega\cdot\hbar\,\omega'\cos(\varphi)=p_e^2c^2$ **1.** equation

and second equation for energy:

$$\hbar\cdot\omega-\hbar\cdot\omega'+m_0\cdot c^2=m\cdot c^2$$

$\hbar^2\cdot(\omega-\omega')^2+2\cdot m_0\cdot c^2\cdot(\hbar\cdot\omega-\hbar\cdot\omega')+m_0^2\cdot c^4=m^2\cdot c^4$ square of previous equation

$\hbar^2\cdot\omega^2+\hbar^2\cdot\omega'^2-2\cdot\hbar^2\omega'\omega+2\cdot m_0\cdot c^2\cdot(\hbar\cdot\omega-\hbar\cdot\omega')+m_0^2\cdot c^4=m^2\cdot c^4$ **2.** equation an additional we can use for total energy $m^2c^4 = p_e^2c^2 + m_0^2c^4$

$(\hbar\,\omega)^2 + (\hbar\,\omega')^2 - 2\hbar\omega\cdot\hbar\omega'\cos(\varphi) = p_e^2c^2$ **1.** equation

$(\hbar\cdot\omega)^2 + (\hbar\cdot\omega')^2 - 2\cdot\hbar^2\omega'\omega + 2\cdot m_0\cdot c^2\cdot(\hbar\cdot\omega - \hbar\cdot\omega') + m_0^2\cdot c^4 = m^2\cdot c^4$ **2.** equation

After the substitutions and simplifications we have the formulas to calculate the shift of wavelength for Compton effect:

$$(1-\cos(\varphi))\cdot\frac{\hbar}{m_0\cdot c^2} = \frac{1}{\omega'} - \frac{1}{\omega}$$

and finally:

$$\Delta\lambda = \lambda_0\cdot(1-\cos\varphi)$$

the parameter

$$\lambda_0 = \frac{h}{m_0\cdot c} = 0{,}024\text{ A}$$

is a Compton's wavelength.

As you see the Compton's wavelength is quit little it is means that the maximal change of X-ray wavelength is equal to **$2\lambda_0$** is a little parameter too. The Compton effect is practically traceable only if the test wavelength **λ** is small. Compton used in his experiments X-ray with wavelength **0,71** Å.

<u>Now we can do some important conclusions about the properties of waves and particles.</u>

There is a two different types of objects in nature:

First one is a waves. Waves are characterized by such phenomena as diffraction (It is defined as the bending of waves around the corners of an obstacle or aperture into the region of geometrical shadow of the obstacle) and interference (Interference is a phenomenon in which two waves superpose to form a resultant wave of greater, lower, or the same amplitude). Wave is not localized phenomenon. We can not define the exact position of wave but only the amplitude of oscillations on different points of matter. Very important that the wave diffraction can be observed only if the size of obstacles is comparable or less than the length of wave. If the wavelength is much smaller than the size of the obstacle, the wave can behave like a particle.

The second is a particles. Unlike waves, particles are well localized. In classical physics, the position of particles can be accurately calculated according to Newton's second law. Phenomena such as diffraction and interference cannot be applied to particles. It is very difficult to present the interference of two chairs or car diffraction around the pillar.

In classical physics, these two objects (particles and waves) are qualitatively different and never cannot be combined. But what picture do we have from the beginning of the last century, when the development of new physics began? The electromagnetic wave demonstrated the wave behavior and at the same time it can be presented as a set of particles-photons. This phenomenon is commonly known as wave–particle duality, which means that a particle of matter can be described as a wave and particle simultaneously. Is it possible to test this hypothesis for electrons? Is the electron can demonstrate the duality wave-particle?

According to the proposal (1924) of the French physicist Louis de Broglie, electrons and other particles have wavelengths that are inversely proportional to their momentum.

$$\lambda = h/mv$$

for photons the same formulas can be obtained:

$$E=m\cdot c^2=h\cdot \nu, p=m\cdot c, \text{ mass of photon can be calculated by this way } m=\frac{h\cdot \nu}{c^2}, p=\frac{h}{\lambda}$$

Further electron diffraction experiments experiments prove the validity of these assumptions.

It means that there is no pure particles or pure waves in the universe. There is only complex objects demonstrated the dual wave-particle behavior. But now we have the next questions.

1. How we have to describe the motion and properties of this new strange objects. What about the trajectory of electrons in this case?

The answer was founded later in quantum mechanics. With each particle associated so called wave function denoted as $\psi(x,y,z,t)$. The wave function can be found as a solution to the Schrödinger equation. How it looks like we will see later.

Like the function describing the waves for free electrons is looks like so: $\psi(x,y,z,t)=A\cdot e^{i\left(\vec{k}\cdot\vec{r}-\frac{E}{h}\cdot t\right)}$. There is different interpretations of wave function but we accept the classical one. $|\psi(x,y,z,t)|\cdot dV$ - is a probability to find the particle inside of volume dV. It is clear that in this case $\iiint_{-\infty}^{+\infty} |\psi(x,y,z,t)|^2 \cdot dV = 1$ it means that particle is exist somewhere in our universe (function is normalized on unit).

As you see the wave function have a pure statistical interpretation. We can not find the exact position of particle but we can find the particle in the fixed position with some probability. The quantum theory have a statistical nature. And we need to use statistical methods to describe the physical properties. In quantum mechanics, only average values of physical quantities can be calculated. The general formulas for that is:

$$<A>=\iiint_{-\infty}^{+\infty} \psi(x,y,z,t)^* \cdot \hat{A} \cdot \psi(x,y,z,t) dV$$

Here $\hat{A}$ is so called operator describing the physical properties of particle. In quantum mechanics, every classical physical parameter is associated with an operator. For example, instead of energy we need to use the Hamilton operator. Instead of momentum we need use momentum operator, and so on. Using the previous formulas, we can calculate the average values of the operators, which can be interpreted as real values, which can be measured.

Trajectory of particles do not exist and can not be precalculated. Only the probability to find particle in given point can be calculated.

2. But as we know from classical mechanics the exact trajectory of particles is exist at can be calculated within the Newton's laws. Paradox? What theory is more general, quantum or classical?

<u>Answer is:</u> of course quantum theory is more general. Classical mechanics can be represented as a special case of quantum theory, as a limit of it.

But how is looks like the criteria of using or not of quantum mechanics? When we already need to use it and when not yet? This criteria exist. This is a <u>*Heisenberg uncertainty principle*</u>. <u>**All objects in universe are quantum!!!**</u> And actually we always need the quantum mechanics to describe its properties. But if the accuracy of physical measurements is not high enough to detect the quantum properties of objects, we can use simple equations from classical theory instead of quantum mechanics.

<u>But question is:</u> when quantum properties begin to manifest and we need start to use the quantum theory instead of classic mechanics?

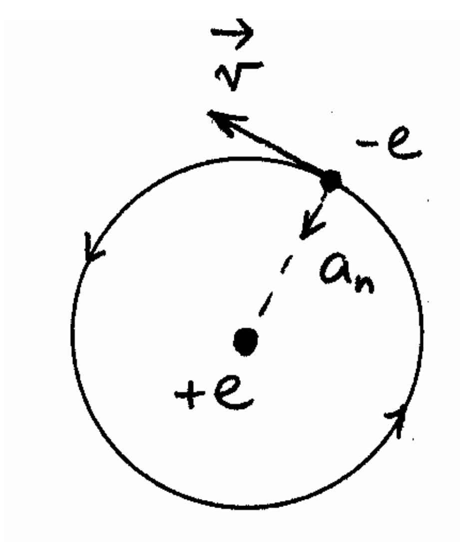
The Heisenberg uncertainty principle can be used for this aim:

$$\Delta x \cdot \Delta p_x \geq h$$

here Δx and Δp_x is a uncertainty of coordinate and momentum. I our case it can be interpreted as a precision of measurements of coordinates and momentum.

Examples:

1. We have the body with mass 50 kg. The position of it can be defined with precision around 1A=10^{-10}м on the edge of measurement capabilities. In order to detect the quantum properties of this body, we need to measure the velocity with an accuracy around 10^{-23}m/s. Very high precision. It means that the quantum properties of this macro objects can not be detected (the quantum properties are beyond the accuracy of our measuring instruments). We need just to increase the precision of measurements. And it can be considered as a classic object.
2. Electron moving around atom. Diameter of atom is around 1A. Mass around 10^{-30}kg. The quantum properties of electrons can be manifested if we measure its velocity with precision 1000 km/s. It is very simple to do. Electron is a pure quantum object and we need to apply the quantum mechanics in this case. Even very rough measurements can detect its quantum nature.



<u>Bohr theory for Hydrogen atom.</u>

This a semiclassical theory which allowed to describe the regularities of spectrum of hydrogen atom. We assume that the electron moves around a proton under the influence of Coulomb force and the II Newton law is looks like so in this case:

$$m \cdot a_n = F_c = \frac{1}{4\pi\epsilon_0} \cdot \frac{e^2}{r^2}$$

This is a purely classical equation that cannot be used directly to describe the motion of a pure quantum object, such as an electron. Bohr used a mixed quaziclassical approach for the hydrogen atom. The quantum properties of an electron were taken into account by introducing into the theory an additional quantization condition. He supposed that the angular momentum of electron must have a discrete values and can be calculated so:

$$m \cdot v \cdot r = n \cdot h$$

Now we have a complex of two equations that can be used to describe the motion of an electron around a nucleus.

$$m \cdot v^2 = \frac{1}{4\pi\epsilon_0} \cdot \frac{e^2}{r}, \; m \cdot v \cdot r = n \cdot h$$

After substituting speed $v = n \cdot h / m \cdot r$ from the second equation into the first we get the expression for the radius of stationary orbits for electron:

$$r_n = \frac{h^2}{m \cdot b \cdot e^2} \cdot n^2 \text{ here } b = \frac{1}{4\pi\epsilon_0}$$

As you see the radius is a discrete parameter and depend on only from n. The of first Bohr orbit **n=1** is equal to

$$r_0 = \frac{h^2}{m \cdot b \cdot e^2} = 0{,}53\, A$$

And has the name Bohr radius.
The speed of electron can be calculated within the framework of Bohr model:

$$v_n = \frac{b \cdot e^2}{h} \cdot \frac{1}{n}$$

The speed of electron on the first Bohr orbit is $v_1 = b \cdot e^2 / h = 2{,}2 \cdot 10^6\, m/s$. The latter gives an idea of the electron velocity in atoms.
Now we ready to calculate the total energy of electron for stationary states. The classical equation can be used: the kinetic energy $\frac{m \cdot v^2}{2}$ and potential (this is potential energy of two interacting point charges) $\frac{-b \cdot e^2}{r}$ and the total energy is equal to:

$$E=\frac{m\cdot v^2}{2}-\frac{b\cdot e^2}{r}$$

Because of ring orbit $b*e^2/r = mv^2$ the total energy can be presented in the next simple form:

$$E=-\frac{m\cdot v^2}{2}$$

After the substitutions and simplifications we get:

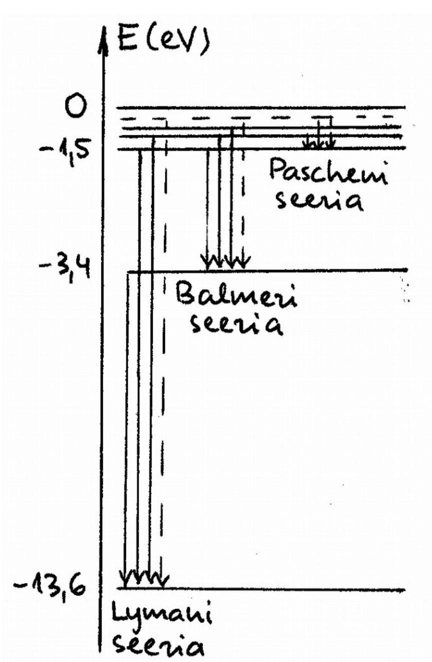
$$E_n=-\frac{m\cdot b^2\cdot e^2}{2\cdot h^2}\cdot\frac{1}{n^2},\ \ n=1,2,3,\ldots$$

As you can see, the energy of stationary states of electron also depends on one integer number n. Since there were other similar dependencies, such integers began to be called quantum numbers.

This equation can be used to explain the basic regularities of the spectrum of hydrogen atom.

By knowing the energy, we calculate the spectrum of the hydrogen at the transition p → n (from p-level to n-th level). The frequency of the emitted photon is calculating so:

$$\omega=\frac{E_p-E_n}{h}=\frac{m\cdot b^2\cdot e^4}{2\cdot h^3}\left(\frac{1}{n^2}-\frac{1}{p^2}\right)$$



Compared to the Balmer formula, the Rydberg constant equals:

$$R=\frac{m\cdot b^2\cdot e^4}{2\cdot h^3}$$

Using this constant, we can write energy more briefly

$$E_n=-R\cdot h\cdot\frac{1}{n^2}$$

Next, we will provide a diagram for stationary states of electron in hydrogen atom and explain the generation of spectral lines by hydrogen atom.

The **Lyman series** arises from electron transitions from higher levels to the lowest energy states. In this case n=1 and p>n

The **Balmer series**, located in the visible spectrum, is arises as the result of transition of electron from higher states to the second energy level. Now n=2 and p>n

And so on.

Finally, we can find hydrogen ionization energy. This is the minimum energy that must be given to the electron to remove it from the hydrogen atom (a free proton-electron system is produced). The electron is no longer proton bound as the total energy of the electron E ≥ 0. Therefore, the ionization energy is: $E_i = R \cdot h = 13{,}6\ eV$.