

Quantum mechanics

Reason for creation:

- Around 1900, some problems in physics could not be explained within the framework of classical physics:
- Blackbody radiation, photoelectric effect, line spectrum of an atom

Blackbody radiation

- Emission of radiation emitted by a black body (absorbs all incident radiation and reflects none)

Wien's displacement law:

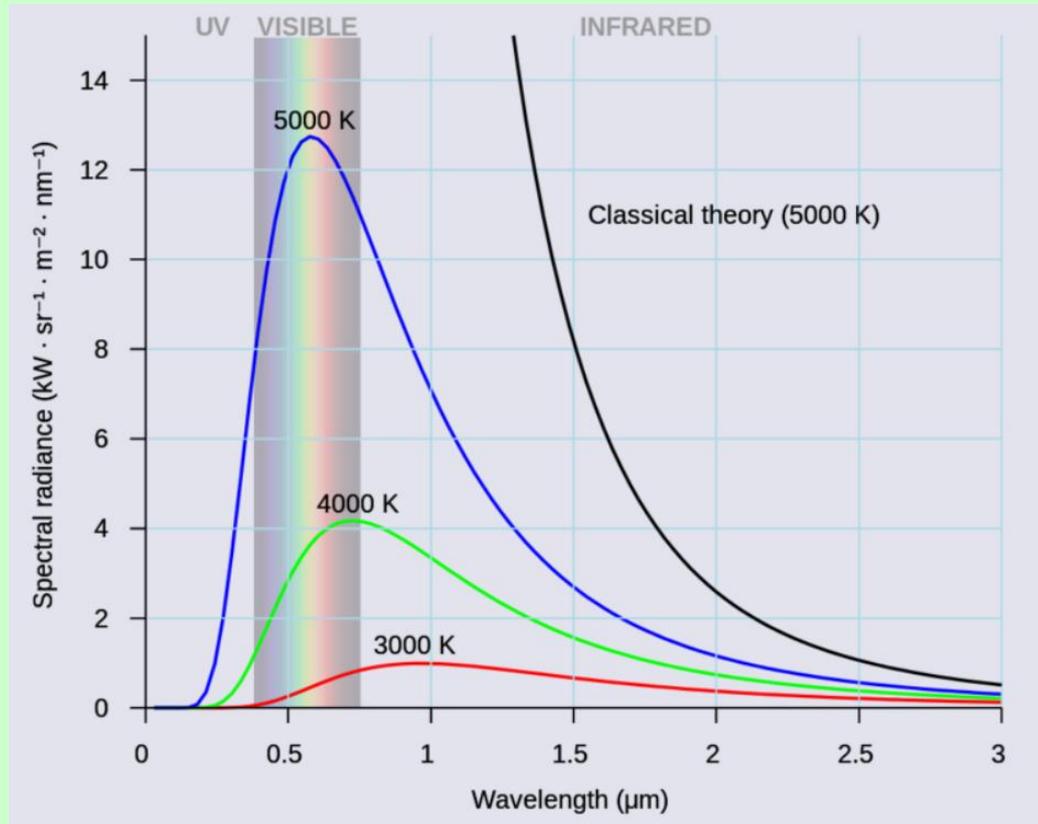
- The wavelength λ_{\max} that corresponds to the radiation with the highest intensity is inversely proportional to the thermodynamic temperature of the blackbody: $\lambda_{\max} = b / T$, where Wien constant $b = 2.898 \cdot 10^{-3} \text{ m.K}$

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Stefan-Boltzmann law:

- The intensity of the blackbody radiation M_e is directly proportional to the fourth power of the thermodynamic temperature T of the blackbody:

$M_e = \sigma \cdot T^4$, where Stefan-Boltzmann constant $\sigma = 5.67 \cdot 10^{-8} \text{ W} \cdot \text{m}^{-2} \cdot \text{K}^{-4}$



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Example 10.2:

Every second, the Earth emits from every square metre of its surface an energy flux of $M_e = 90.854 \text{ J}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ in the form of electromagnetic radiation. At what temperature t would the same amount of energy be emitted by an equally large absolute black body?

$[T \approx 200 \text{ K} \Rightarrow t \approx -73 \text{ }^\circ\text{C}]$

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Planck's theory:

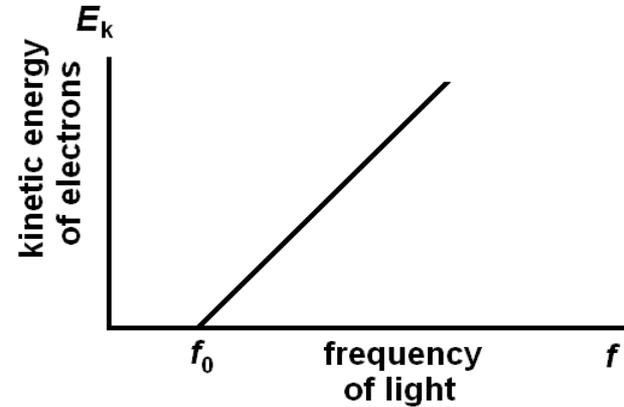
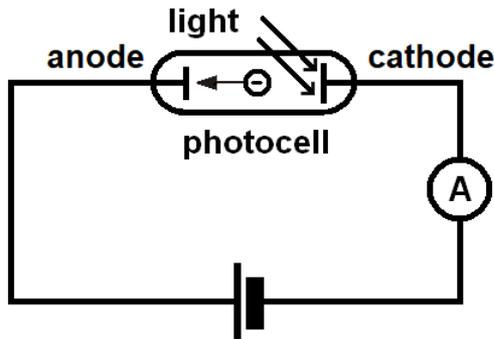
- The energy of light (or electromagnetic waves) does not propagate continuously, but in energy quanta - photons
- The quantum of energy radiated or absorbed is directly proportional to the frequency of the radiation: $E = h f$,
where $h = 6.626 \cdot 10^{-34}$ J.s is Planck constant
- By analogy, electrons bound in an atom or in a solid cannot acquire arbitrary energies but only certain
- They are at certain energy levels and to move to another energy level they must accept or give up energy corresponding to the energy difference between the levels depending on whether they move to a higher or lower energy level

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External photoelectric effect

- In solids (metals) on which electromagnetic radiation is incident, electrons are released from their structure – so-called photoemission of electrons occurs
- At the end of the 19th century it was not clear why electrons were only released from matter at higher frequencies of radiation and why radiation of lower frequencies did not release electrons from bodies even at high intensities
- Classical physics predicted that the higher intensity of the incident radiation should make the electrons inside the metal vibrate more and they should be able to leave the structure more easily

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- Experimentally, by studying the photoelectric effect, it was found:

1. For each metal there is a certain cutoff frequency f_0 . If the frequency f of the incident radiation is less than the cutoff frequency f_0 , the radiation is unable to release electrons from the metal. Radiation with a frequency $f \geq f_0$ releases electrons from the metal

2. For $f \geq f_0$, the number of electrons released is directly proportional to the intensity of the incident radiation

3. The energy of the released electrons is directly proportional to the frequency of the incident radiation and does not depend on the intensity of the incident radiation

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Einstein's theory of the photoelectric effect - 1905 - proof of the quantum nature of electromagnetic radiation - Nobel Prize in Physics 1921:

- Each released electron absorbs one quantum of energy: $E = h f$

- $h f = W + \frac{1}{2} m_e v^2$, where W is the output work required to release the electron from the metal and $\frac{1}{2} m_e v^2$ is the kinetic energy of the released electron

- The photoelectric effect occurs if the quantum of radiation energy absorbed by the electron is at least equal to the output work $W = h f_0$, where f_0 is the cutoff frequency of the metal at which the photoelectric effect occurs

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Example 11.6:

Determine the limiting value of the wavelength λ_0 of the photoelectric effect for silver, whose output work $W = 4.74$ eV.

$[\lambda_0 \approx 262 \text{ nm}]$

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Photon

- The quantum nature of electromagnetic radiation is manifested not only in the emission and absorption of radiation but also in its propagation through space
- I.e. electromagnetic radiation propagates in the form of single quanta of electromagnetic waves – so-called photons
- A photon behaves like a particle that has zero rest mass m_0 and moves at speed c (the speed of light in a vacuum)
- Photon energy: $E = h f = h c / \lambda$, where λ is the wavelength of the relevant electromagnetic radiation in vacuum
- The motion mass of the photon m – from the relation $E = mc^2$
- Photon momentum: $p = m c = h / \lambda$

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- Light quantum - a photon behaves like a particle and at the same time is characterized by a wavelength and is subject to all the laws of waves – a manifestation of the corpuscular wave dualism of electromagnetic radiation
- Electromagnetic radiation has a dual nature - it manifests simultaneously as waves (interference, bending, refraction, polarization) and as a stream of photons (emission and absorption of energy)

Wave properties of particles

- The waves can be described using quantities characteristic of particles (mass, energy, momentum)
- However, according to Louis de Broglie, the quantities characteristic of waves can also be used to describe the motion of particles

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- The de Broglie relationship: $\lambda = \frac{h}{p} = \frac{h}{mv}$
- Each particle of momentum p is associated with a wave (de Broglie wave) of wavelength λ

Example 11.5:

Determine the de Broglie wavelength λ of a proton with kinetic energy

$E_k = 15$ eV. The mass of the proton is $m = 1.67 \cdot 10^{-27}$ kg.

[$\lambda = 7.4 \cdot 10^{-12}$ m]

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Wave function

- In quantum mechanics it is impossible to determine the exact trajectory along which a particle moves
- We can only determine the probability with which the particle is in the vicinity of the point with coordinates x, y, z at time t
- This probability is determined by the wave function $\Psi(x, y, z, t)$, which expresses the dependence of the amplitude of the de Broglie wave on the spatial coordinates and on time

Quantum mechanics

- $|\Psi(x, y, z, t)|^2$ – probability density of particle occurrence at time t in the vicinity of the point with coordinates x, y, z
- A higher probability density implies a higher probability of a particle occurring at a given time and location
- The values of the wave function $\Psi(x, y, z, t)$ can be determined from the equation of motion for waves – the so-called Schrödinger equation – the key mathematical formulation of quantum mechanics

Quantum mechanics

Bohr's model of the atom

- Arose as a result of a problem in spectral analysis unexplained by classical physics
- Spectral analysis detects the wavelengths of radiation emitted by a particular source
- From here, information on the chemical composition and temperature of the source can be obtained
- Spectra are produced e.g. by radiation or emission of heated bodies – so-called emission spectra
- Heated solid or liquid bodies emit a continuous spectrum ⇒
⇒ a continuous colour band in which one colour band transitions continuously into a band of the following colour
- However, in low-temperature plasmas (e.g. ionized gases) we observe a line spectrum, which is evidence of light emission of certain well-defined wavelengths

Quantum mechanics

- The line spectrum cannot be explained by classical physics
- Rutherford discovered the atomic nucleus \Rightarrow the origin of the planetary model of the atom:
- The heavy nucleus had a position similar to that of the Sun and the light electrons had a position similar to that of the planets

2 fundamental flaws of the planetary model of the atom:

1. The electrons would lose energy by radiation and in a fraction of a second they would hit the nucleus - the atom would not be stable
2. The spectrum of radiation emitted by an atom would not be linear but continuous

Solving the line spectrum problem:

Niels Bohr developed the first quantum model of the hydrogen atom in 1913

Quantum mechanics

3 Bohr's postulates:

I. Of all the possible circular motions of the electron around the nucleus allowed by classical mechanics, are stable only those whose radii r satisfy the condition

$$2 \pi m r v = n h, \text{ where } n \text{ is natural number}$$

II. When moving along a path that satisfies the first postulate, the electron loses no energy

- this assumption is contrary to classical electrodynamics, according to which an electron moving along a curved path should radiate energy
- the energy of the electron would steadily decrease until it hit the nucleus
- the processes inside atoms, however, are governed by different laws than the macrophysical processes dealt with by classical physics

Quantum mechanics

III. When an electron passes from the higher orbit of quantum number n_2 to the lower orbit of quantum number n_1 , the atom emits a photon of

frequency f for which: $f = \frac{E_{n_2}}{h} - \frac{E_{n_1}}{h}$,

where E_{n_1} respectively E_{n_2} are the energies of the electron in the n_1 -st respectively n_2 -nd orbits

- For a hydrogen atom is $f = -\frac{me^4}{8\varepsilon_0^2 h^3} \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right)$, where ε_0 is vacuum permittivity

- Quantization of the radius of electron orbits \Rightarrow the energy of the atom is quantized

- If the shell of an atom absorbs or radiates energy, its energy does not change continuously but in quanta

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- The energy of the photon $E = h f$ of electromagnetic radiation, which the hydrogen atom emits respectively absorbs during the transition of the electron from the orbit n_2 to the orbit n_1 respectively from the orbit n_1 to the orbit n_2 , is equal to the difference of energies of the electron on these orbits

- Therefore:
$$E = hf = E_{n_2} - E_{n_1} = -\frac{me^4}{8\varepsilon_0^2 h^2} \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right)$$

- If an electron moves from a higher energy (and larger radius) orbit to a lower energy (and smaller radius) orbit, the atom radiates energy

- If an electron moves from a lower energy (and smaller radius) orbit to a higher energy (and larger radius) orbit, the atom absorbs the energy

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How was the relationship for the energy of the electron at the n -th level

established $E_n = -\frac{me^4}{8\varepsilon_0^2 h^2} \cdot \frac{1}{n^2}$?

- An electrostatic force described by Coulomb's law acts on the electron, which acts as a centripetal force \Rightarrow the electron moves in a circle:

$$F_e = F_d \Leftrightarrow \frac{1}{4\pi\varepsilon_0} \cdot \frac{e^2}{r^2} = \frac{mv^2}{r} \text{ (a), next, from Bohr's 1-st postulate}$$

$2\pi m r v = n h$ we express the velocity and plug it into the equation (a)

- From here we express the radius of the circular path (the so-called Bohr

radius): $r_n = \frac{n^2 h^2 \varepsilon_0}{\pi m e^2}$ (b); for the electron of hydrogen in the base state

($n = 1$): $r_1 = 5.3 \cdot 10^{-11}$ m

Quantum mechanics

kinetic energy of the electron using the equation (a): $E_k = \frac{1}{2}mv^2 = \frac{e^2}{8\pi\epsilon_0 r}$

- The potential energy of a hydrogen atom corresponds to the work done by the electric force to move an electron from infinity to a distance r from

the proton: $E_p = \int_{\infty}^r F_e \cdot d\mathbf{r} = \frac{e^2}{4\pi\epsilon_0} \int_{\infty}^r \frac{1}{r^2} \cdot d\mathbf{r} = -\frac{e^2}{4\pi\epsilon_0 r}$

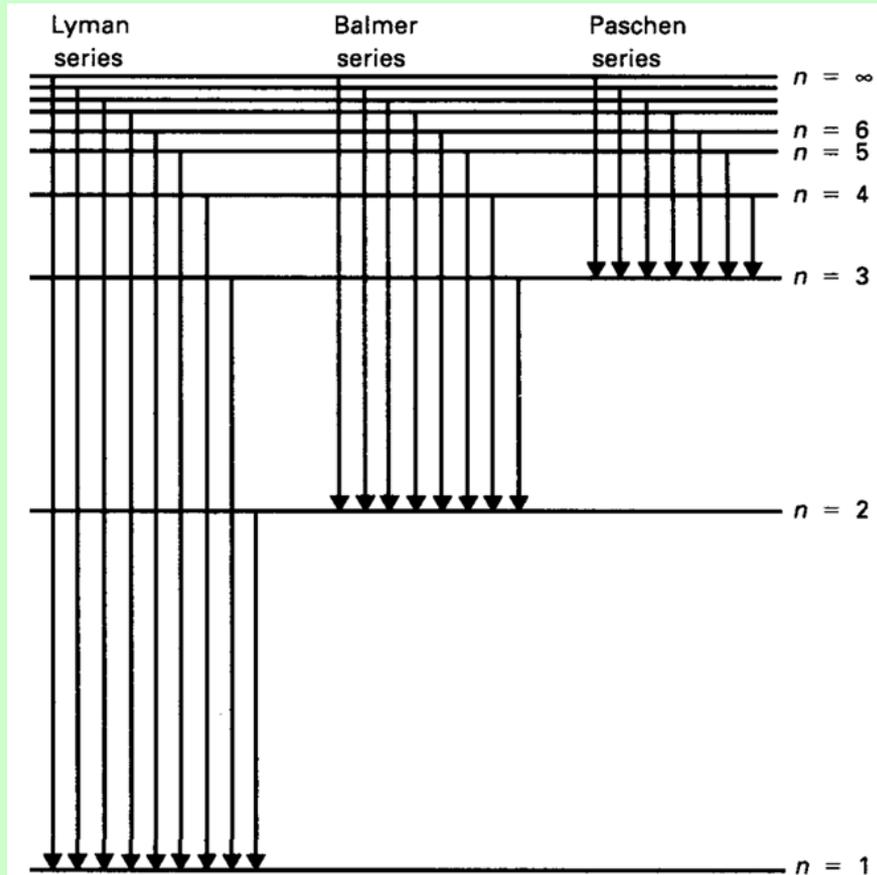
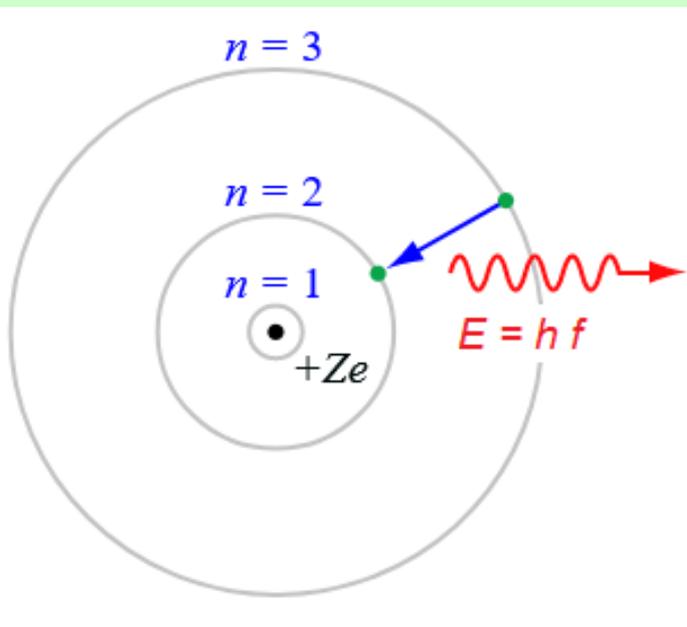
- Total energy of the electron: $E = E_k + E_p = -\frac{e^2}{8\pi\epsilon_0 r}$ (c)

- From (b) to (c) and we get $E_n = -\frac{me^4}{8\epsilon_0^2 h^2} \cdot \frac{1}{n^2}$

- For the electron of hydrogen in the base state ($n = 1$) is $E_1 = -2.17 \cdot 10^{-18} \text{ J}$
= - 13.6 eV – the so-called ionization energy to release the hydrogen electron from the base state

Quantum mechanics

- Each energy level is characterized by a quantum number n
- The lowest level has $n = 1$, the next $n = 2$, etc.
- The energy of a level that has $n = \infty$, is 0
- The spectrum of each atom has several characteristic series of lines
- The hydrogen spectrum has three main series of lines (Lyman, Balmer, Paschen)



Quantum mechanics

Refinement of Bohr's theory, quantum numbers

- A more detailed and precise study of the line spectra of the gases showed:
- The individual lines are not simple, but that each of them is composed of multiple lines – the so-called fine structure of spectral lines
- Bohr's ideas had to be refined:

The conclusions of quantum theory imply that not only the energy of the electron is quantized in the shell of the atom, but also its angular momentum, the magnetic moment of the corresponding motion around the nucleus and also the spin

- To fully describe the motion state of an electron in the shell of an atom, four quantum numbers are needed:

n – main quantum number, determines energy quantization,

l – secondary (orbital) quantum number, determines the quantization of angular momentum,

m – magnetic quantum number, determines the magnetic moment quantization,

s – spin quantum number, determines the quantization of the electron's own angular momentum – spin