Atomic spectra. Bohr model. Atomic physics.

An atom is the smallest constituent unit of the substance carrying the properties of a certain chemical element. Every atom is composed of a **nucleus** and one or more **electrons** bound to the nucleus. The nucleus consists of one or more **protons** and typically a similar number of **neutrons**. Protons and neutrons are called **nucleons**. The protons have a positive electric charge ($+e$), the electrons have a negative electric charge ($-e$), and the neutrons have no electric charge. The integrity of the atom is based on the attractive electric forces acting between the positive nucleus and negative electrons. The dimensions of atoms are of some angstroms (Å) by the order of magnitude (1 Å = 10^{-10} m, *Anders Ångström*, Swedish physicist). The dimensions of nuclei are of some femtometers (1 fm = 10^{-15} m). More than 99.9% of the mass of an atom mass is located in the nucleus because the mass of a proton $m_p = 1836.1\ m_e$, the mass of a neutron $m_n = 1838.7\ m_e$, where the mass of an electron $m_e = 9{,}11 \cdot 10^{-31}$ kg. If the numbers of protons and electrons are equal, that atom is electrically neutral. If an atom has more or fewer electrons than protons, then it has an overall negative or positive charge, respectively, and is called an ion.

The planetary model of the atom is based on the imagined similarity between the atom and the Solar system. The nucleus is playing the role of the Sun. The electrons are playing the role of the planets. The planetary model is very widely used but we must take into account that the trajectories of the electrons are just a human imagination only. As a result of the **Heisenberg uncertainty principle,** the electrons cannot possess the trajectories because the coordinate and the momentum of an electron can not have exact values at the same time. The motion of the electrons in the atom is neither translation nor rotation. It is really a standing wave or an oscillation. Here we are talking about the matter waves (de Broglie waves) and the principle of the **wave-particle duality**.

The Bohr model of the hydrogen atom (*Niels Bohr*, Danish physicist) assumes that the planetary atom can exist in some **stationary** states (that is, is not changing in time). The energy of the atom in the stationary state is constant and the stationary atom is not emitting electromagnetic waves (the 1st postulate of Bohr). The atom is emitting or absorbing the electromagnetic waves by the transition from one stationary state to the another (the 2nd postulate of Bohr). The experimental evidence of the validity of the Bohr model is the presence of **series** on the emission spectra of hydrogen. The spectral series can be described by the **quantum numbers**. They are integer or half-integer numbers determining the values of physical quantities in the atomic or nuclear physics.

The Balmer-Rydberg formula is determining the wavelengths λ or photon energies $h f$ for the emission spectral lines of the hydrogen atom: $1/\lambda = R_H \{(1/n_f^2) - (1/n_i^2)\}$ or $h f = R \{(1/n_f^2) - (1/n_i^2)\}$, where n_f (final) ja n_i (initial) are integer quantum numbers. The wavenumber $R_H = 1.097 \cdot 10^7\ \text{m}^{-1}$ is called **Rydberg constant** and the energy $R = 13.6$ eV (also 1 Ry) is called **Rydberg energy** (*Johannes Rydberg*, Swedish physicist). The quantum number of the final state n_f is determining the certain spectral series. For example, the Lyman series located in the ultraviolet part of the spectrum is described by $n_f = 1$, the Balmer series consisting of visible spectral lines has $n_f = 2$ etc. The quantum number of the initial state n_i is connected with the certain spectral line inside the series. Everywhere $n_i > n_f$. For the most intensive line (α-line) of some series, we have $n_i = n_f + 1$. For the series, the limit is valid $n_i = \infty$. Because the energy of the radiated photon must be a difference between the energies of the initial (E_i) and final (E_f) states of the hydrogen atom: $h f = E_i - E_f$, we can rewrite the Balmer-Rydberg formula in the following way: $h f = R \{(1/n_f^2) - (1/n_i^2)\} = (-R / n_i^2) - (-R / n_i^2)$ and come to the conclusion that the energy of the atom is inverse proportional to the quantum number n squared: $E_n = -R / n^2$ where R is the Rydberg energy.

The parameters of the stationary states according to the Bohr model are based on the fact that the angular momentum of the electron is equal to the product of quantum number n and the reduced Planck constant $\hbar = h/(2\pi) = 1.054 \cdot 10^{-34}$ J·s : $L_n = n\,\hbar$. The quantum number of the state n decreases by one by the emission of photon and it increases by one by the absorption because the momentum of the photon $\hbar k$ is either removed from the atom (emission) or added to it (absorption).

The net energy of the atom E_n (depending on the quantum number n) is negative according to the negative value of the potential energy E_p originating from the attractive electric force between the nucleus (only one positive proton) and the negative electron: $E_p = -k\, e^2/r_n$. The product of charges of the proton ($+e$) and electron ($-e$) is negative ($-e^2$). The constant $k = 9 \cdot 10^9$ N$\cdot$m^2/C^2 used in the Coulomb's law and the mean distance between the proton and electron r_n are also included in the formula for E_p. According to the Newton's 2nd law, we get for the absolute value of the attractive electric force in the hydrogen atom the formula $F = m\, a_c = m\, v^2/r$, where a_c is the centripetal (normal) acceleration of the electron. On the other hand, the inverse potential energy $-E_p = F \cdot r = m\, v^2 = 2\, E_k$. So we get for the net energy $E_n = E_k + E_p$ the formula $E_n = E_k + (-2\, E_k) = -E_k$. According to the formula $E_n = -R/n^2$, we have for the ground state ($n = 1$): $E_1 = -R = -13.6$ eV. All together $E_k\,(n = 1) = m\, v_1^2/2 = R$ and we get $v_1 = (2R/m)^{1/2}$ or $v_1 = 2.188 \cdot 10^6$ m/s = 2188 km/s using the value of the mass of the electron $m_e = 9.109 \cdot 10^{-31}$ kg.

The speed, radius of the orbit and the angular velocity of the rotating electron according to the Bohr model. From the formula of the kinetic energy $E_k = mv^2/2$ and the formula for the net energy $E_n = -R/n^2$, we can conclude that the imagined speed v of the electron must depend on the quantum number n in the inverse proportional way: $v_n = v_1 / n$. Because the potential energy E_p itself depends on the distance between the proton and electron r_n (radius of the orbit) in the inverse proportional way ($E_p = -k\, e^2/r_n$), the r_n must be proportional to the quantum number n squared: $r_n = r_1\, n^2$, where r_1 is the radius of the imagined orbit of the electron in the ground state of the atom. It is called **Bohr radius**. From the formula $E_p\,(n = 1) = -k\, e^2/r_1 = -2\, E_k = -2R$ we can derive the formula $r_1 = k\, e^2/R = 5.29 \cdot 10^{-11}$ m ≈ 0.53 Å. Using the values of v_1 and r_1 , we get $L_1 = m\, v_1\, r_1 = 1.05 \cdot 10^{-34}$ J$\cdot$s $= \hbar$ and $L_n = m\, v_n\, r_n = m\,(v_1/n)\,(r_1\, n^2) = n\,\hbar$. The imagined angular velocity $\omega_n = v_n / r_n = (v_1/n)\,(r_1\, n^2)^{-1} = (v_1/r_1) / n^3 = \omega_1 / n^3$ and so the imagined frequency of rotation f_n is inverse proportional to the cube of a quantum number: $f_n = f_1 / n^3$. The imagined frequency of rotation in the ground state is $f_1 = 6.58 \cdot 10^{15}$ Hz = 6580 THz.

The electron orbits have certain defined radii according to the Bohr model because the principle of the wave-particle duality is valid. The electron possessing the linear momentum p has the wavelength $\lambda = h / p$ (de Broglie formula). The matter wave of the electron must be in the constructive interference with itself. So the part of the electron wave which is already performed one rotation (cycle) along to the circular orbit must be in the constructive interference with the another part not yet performed this cycle. According to this requirement on the length of the orbit $2\pi\, r_n$ must fit an integer number n of wavelengths λ_n . This number is actually the quantum number n.

The electron in the many-electron atom is described by the four quantum numbers: n, l, m and s. The distance of the electron with respect to the nucleus is determined by the main quantum number n, used already in the Bohr model. In the chemistry it is called the number of the electron shell. The spatial form of the standing wave of the electron is called **orbital**. The type of the orbital is described by the orbital quantum number l. The orbitals are typically denoted by the letters s ($l = 0$), p ($l = 1$), d ($l = 2$), f ($l = 3$) etc. So we talk about the s-, p-, d- or f-electrons and the quantum number n is standing before the letter (2p- or 3d-electron, for example). The length of the vector $\boldsymbol{l}$ of the orbital angular momentum of the electron is determined by the quantum number l according to the formula: $|\boldsymbol{l}| = \hbar\, [l\,(l + 1)]^{1/2}$. The position of the vector $\boldsymbol{l}$ (the axis of the orbital) with respect to the direction of the magnetic field acting on the electron is determined by the magnetic quantum number m. The length of the projection of the orbital angular momentum vector $\boldsymbol{l}$ on the direction of the magnetic field (obviously called z-axis) is determined by the formula $l_z = m\,\hbar$. Note that the lengths and projections of the angular momentum of the electron are always measured in the units of reduced Planck constant $\hbar$.

The possible values of quantum numbers are: $n = 1, 2, 3, \ldots$; $l = 0, 1, \ldots, n-1$ (the integer numbers between 0 and $n - 1$); $m = -l, \ldots, +l$ (the integer numbers between $-l$ and $+l$). The possible values of spin quantum number s are $-½$ and $+½$. They desribe the two possible orientations of the electron **spin** or the angular momentum of its internal rotation in the magnetic field – one along the field vector **B** and another countrary to this vector.