The Structure of Atoms and the Bohr Model

Having already explored the Plum Pudding model and Rutherford's nuclear atom model through the Geiger-Marsden experiments, we know that the atom consists of a tiny, dense, positively-charged nucleus ($R_C < 10^{-14}$ m, charge $Q = Z \cdot e$) containing most of the atomic mass, surrounded by a much larger electron cloud (10^{12} to 10^{15} times the nuclear volume). This electron cloud contains Z electrons, each with charge $-e$, but contributes negligibly to the total mass.

A key question emerges about the structure of this electron cloud: are the electrons statically distributed or in motion? A static distribution is unstable due to electrostatic attraction to the nucleus. However, moving electrons present their own puzzle - classical electrodynamics predicts that accelerating charges should continuously emit electromagnetic radiation, which would cause them to spiral into the nucleus. This contradicts the observed stability of atoms. Understanding this paradox requires us to consider quantum mechanical effects.

Atomic spectra

In 1859 Kirchhoff and Bunsen observed that atoms absorb light only for particular values of the wavelength. Moreover these wavelength values are specific for the particular kind of atoms and form the absorption and emission spectra of these atoms. Early instruments for recording spectra made use of a prism as diffracting element and a photo plate for recording. The prism gave rise to a rainbow-colored stripe at the plate and narrow dark lines appeared exactly at those positions that correspond to the particular wavelengths of atom absorption. Thus, the photo plates showed dark lines at these positions and those compositions of lines were called *line spectra*. On the basis of further experiments one was able to state:

- For every wavelength at which an atom absorbs light, emission of light is possible if the atom was previously supplied with enough energy

- The absorption and emission spectra are specific for every kind of atom. Thus, one is able to determine the chemical element absorbing or emitting the radiation on the basis of the line spectrum.

- The values of wavelength (spectral lines) are not arbitrarily narrow. They rather exhibit a distribution of intensity. This indicates that atoms do not emit strictly monochromatic radiation.

In 1885 Balmer discovered that the emission spectrum of hydrogen is composed of a series of lines that obey a specific law, namely

$$\frac{1}{\lambda_k} = R_y \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right).$$

In this equation R_y denotes the Rydberg constant ($R_y = 109\,678\ \mathrm{cm}^{-1}$) and n_1 and n_2 adopt only the integers $n_1 = 2$ and $n_2 = 3, 4, 5\,...$. This series of lines with $n_1 = 2$ is called *Balmer series*. Later Lyman and Paschen discovered additional series of the hydrogen emission called *Lyman series* ($n_1 = 1$ and $n_2 = 2, 3, 4\,...$) and *Paschen series* ($n_1 = 3$ and $n_2 = 4, 5, 6\,...$).
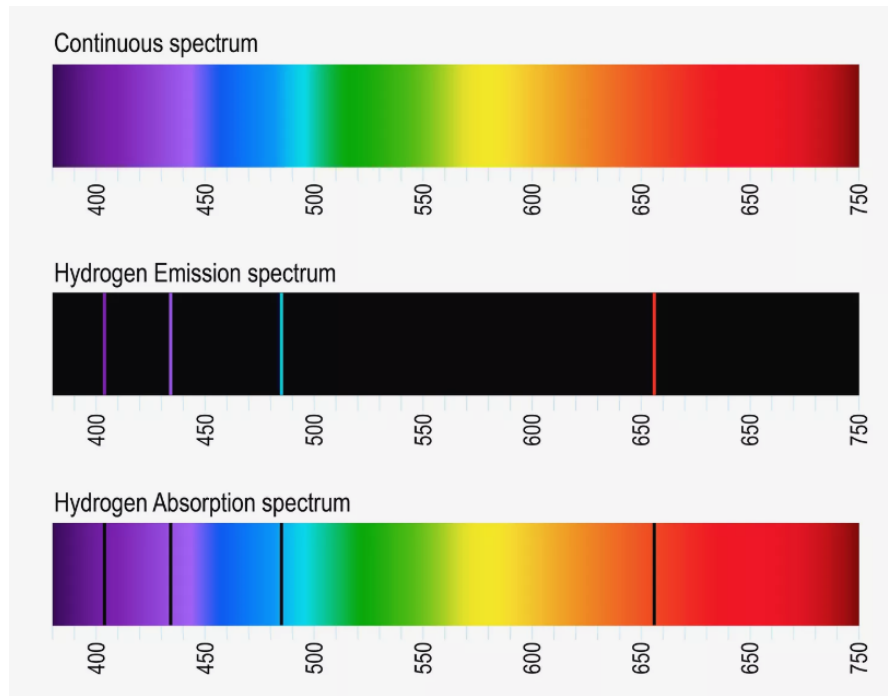

Figure 1: A continuous spectra in the visible range of light (top), a hydrogen emission line spectrum showing narrow lines of light where hydrogen emits (center), and a hydrogen absorption spectra showing black lines where hydrogen absorbs light (bottom). Source: https://www.thoughtco.com/definition-of-balmer-series-604381

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The Bohr model

On the basis of the spectral lines, a number of models for the architecture of atoms were proposed but they were not able to explain all experimental results as a whole. Among them was Bohr's famous model from 1913. In the framework of this model electrons with mass m_e propagate with a velocity v at a circular orbit with radius r around the center of mass of the nucleus-electron system. This system can be described through the motion of a particle with the reduced mass $\mu = m_\mathrm{e} \cdot m_\mathrm{n} / (m_\mathrm{e} + m_\mathrm{n})$ around the center of the Coulomb potential from the nucleus at $r = 0$. The nucleus bears the charge $Q = Z \cdot \mathrm{e}$ and the mass m_n, which is much greater than m_e and gives rise to $\mu \approx m_\mathrm{e}$. From the equilibrium of the centrifugal force and the centripetal force (Coulomb force),

$$\frac{\mu v^2}{r} = \frac{1}{4\pi\varepsilon_0} \frac{Ze^2}{r^2},$$

we can determine the radius of the orbital

$$r = \frac{1}{4\pi\varepsilon_0} \frac{Ze^2}{\mu v^2}.$$

As long as there are no constraints for the energy of the electron $\mu v^2 / 2$, the orbit can adopt every possible radius. However, if we describe the electron through a *matter wave*, then for every stationary state of the atom a corresponding standing wave has to exist. Furthermore, if the wave-like description is supposed to comply with the classical orbit description, then the circumference of the orbital has to be a magnitude of the de Broglie wavelength,

$$2\pi r = n \cdot \lambda_\mathrm{D},$$

with $n = 1, 2, 3, ...$ and $\lambda_\mathrm{D} = h / (\mu \cdot v)$. As a consequence, the velocity of the electron then reads as

$$v = n \cdot \frac{h}{2\pi\mu r}.$$

Now, we can use the expression for the velocity v in the equilibrium of forces and calculate the orbit radius under the constraint of stationary states being described through matter waves,

$$r(n) = \frac{\varepsilon_0 h^2}{\pi\mu e^2} \frac{n^2}{Z}$$
$$= a_0 \frac{n^2}{Z}.$$

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The constant a_0,

$$
\begin{aligned}
a_0 &= \frac{\varepsilon_0 h^2}{\pi \mu e^2} \\
&= \frac{4\pi \varepsilon_0 \hbar^2}{\mu e^2} \\
&= 5.2918 \cdot 10^{-11} \text{ m}
\end{aligned}
$$

represents the **Bohr radius**, which is the smallest radius of the electron orbit $(n = 1)$ within a hydrogen atom with $Z = 1$. Due to the constraint $2\pi r = n \cdot \lambda_{\mathrm{D}}$, the radii of the electron orbitals are limited to discrete values. Thus, they are *quantized*.

Concerning the kinetic energy of an electron $\mu v^2 / 2$ within a discrete orbit, we can make use of the equilibrium of forces and calculate

$$
E_{\mathrm{kin}} = \frac{1}{2} \mu v^2 = \frac{1}{2} \frac{1}{4\pi \varepsilon_0} \frac{Z e^2}{r} = -\frac{1}{2} E_{\mathrm{pot}}.
$$

We can see that the kinetic energy of an electron is equal to $-1/2$ times the potential energy of the electron in the Coulomb potential of the nucleus. The total energy then reads as

$$
E = E_{\mathrm{kin}} + E_{\mathrm{pot}} = -\frac{1}{8\pi \varepsilon_0} \frac{Z e^2}{r}.
$$

We can further use the expression for the discrete radius $r = r(n)$ and get

$$
\begin{aligned}
E(n) &= E_{\mathrm{n}} \\
&= -\frac{\mu e^4}{8 \varepsilon_0^2 h^2} \cdot \frac{Z^2}{n^2} \\
&= -Ry^* \cdot \frac{Z^2}{n^2},
\end{aligned}
$$

with the Rydberg energy (Rydberg constant with respect to energy)

$$
\begin{aligned}
Ry^* &= \frac{\mu e^4}{8 \varepsilon_0^2 h^2} \\
&= h \cdot c \cdot Ry.
\end{aligned}
$$

It is evident that the electron can adopt only particular values of energy E_{n}, which might be expressed in terms of a *quantum number* $n = 1, 2, 3 \dots$. These stationary energetic states

are also called *quantum states* of the atom and the quantum number n is called the *principal quantum number.*

Moreover, it is evident that **the energy is negative** and approaches 0 if the orbital radius approaches $+\infty$, which corresponds to the principal quantum number approaching $+\infty$.
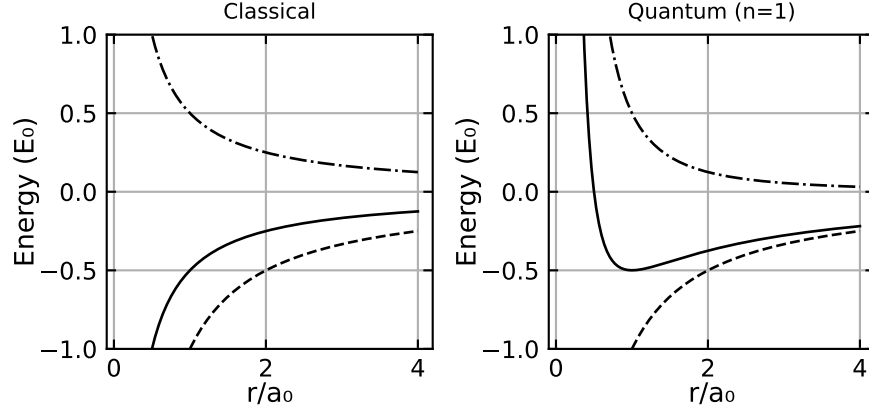

Figure 2: Kinetic energy, potential energy, and total energy of an electron within the Coulomb potential. Left shows classical mechanics and electrodynamics framework. Right shows quantum mechanical correction resulting in minimum total energy.

Please note:

- The particular value of the Rydberg constant depends on the reduced mass of the system electron plus nucleus $1/\mu = 1/m_e + 1/m_c$. In order to use a general constant one defines the Rydberg constant Ry_∞ for an infinite nucleus mass ($m_c \longrightarrow \infty$) with the result $\mu = m_e$. The Rydberg constant for a finite nucleus mass then is given through $Ry = Ry_\infty \cdot \mu/m_e$, with $Ry_\infty = 109737 \text{ cm}^{-1}$

- The Bohr model is a *semi-classical* model. The motion of the electron is treated in the framework of classical mechanics as the motion of a point-like particle within a Coulomb potential plus the additional constraint from the matter wave leading to quantized quantum states.

- From the quantized velocity of the electron $v = n \cdot h/(2\pi\mu r)$ it follows $\mu r v = n \cdot \hbar = \left|\vec{L}\right|$. The *angular momentum* of the electron is also quantized. It can adopt only magnitudes of $\hbar$. Both conditions, the quantization of the electron orbit circumference $2\pi r = n \cdot \lambda_D$ and the quantization of the electron angular momentum $\left|\vec{L}\right| = \mu r v = n \cdot \hbar$ are identical.

In order to explain the shape of the line spectra we have to state a hypothesis. If a photon is absorbed by an atom, then the atom might go from a lower energetic state $E(n_i) = E_i$ to a higher energetic state $E(n_k) = E_k$ under the prerequisite of energy conservation,

$$h \cdot \nu = E_{\mathrm{k}} - E_{\mathrm{i}}.$$

The spectral series of hydrogen correspond to transitions between different energy levels. The main series are:

Table 1: Spectral series of the hydrogen atom showing the initial and final states for each transition series along with the corresponding spectral region.

Series Name	Initial State (n_i)	Final States (n_k)	Spectral Region
Lyman	1	2,3,4,...	Ultraviolet
Balmer	2	3,4,5,...	Visible
Paschen	3	4,5,6,...	Infrared
Brackett	4	5,6,7,...	Infrared
Pfund	5	6,7,8,...	Far Infrared

The energy of the photon is used to compensate the energy difference between state E_{k} and state E_{i}, $\Delta E = E_{\mathrm{k}} - E_{\mathrm{i}}$. From the relation $E_{\mathrm{n}} = -Ry^* \cdot \frac{Z^2}{n^2}$ we obtain

$$\nu = \frac{Ry^*}{h} Z^2 \left(\frac{1}{n_i^2} - \frac{1}{n_k^2} \right).$$

With the aid of $\nu = c/\lambda$ as well as $Ry^* = Ry \cdot c \cdot h$ we get further

$$\frac{1}{\lambda} = Ry \cdot Z^2 \left(\frac{1}{n_i^2} - \frac{1}{n_k^2} \right),$$

which is the general equation for the lines of a line spectrum and comprises the equation stated by Balmer for the special case of hydrogen ($Z = 1$).
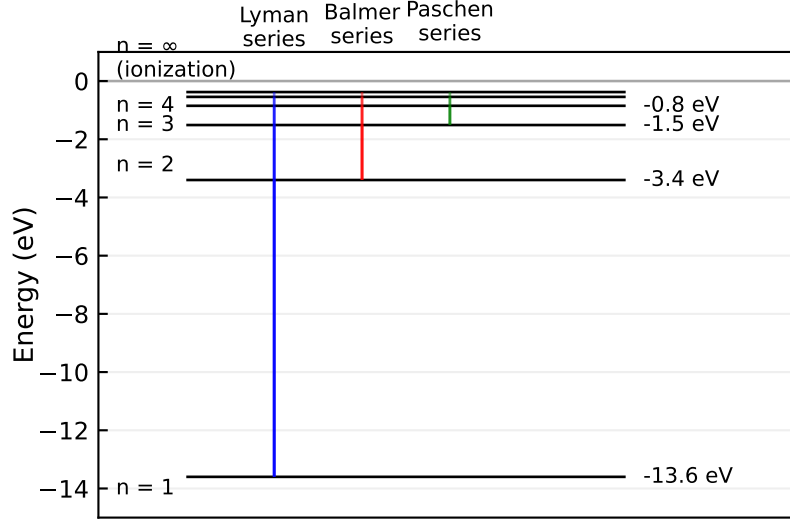
Figure 3: Energy levels and transitions in the hydrogen atom according to the Bohr model.

In summary we can state:

- Electrons propagate in circular orbitals around the nucleus. The radii of the orbital are quantized and the particular radius increases *quadratically* with the principal quantum number n,

$$r_n = \frac{a_0}{Z} \cdot n^2.$$

- The radii are inversely proportional to the atomic number.

- Every quantum state characterized through the quantum number n is associated with a particular *negative* energy E_n,

$$E_n = -Ry^* \frac{Z^2}{n^2}.$$

- The energy for $n \longrightarrow \infty$ and thus $r \longrightarrow \infty$ is set as 0. The difference between E_n and E_∞ is the ionization energy (the energy the electron needs to escape from the Coulomb potential).

- Through absorbing a photon of energy $h \cdot \nu$ the atom goes from a lower energetic state E_i into a higher energetic state E_k, if conservation of energy is fulfilled.

> **i** The Bohr-Sommerfeld Model: A Quantum Mechanical Bridge

The Bohr-Sommerfeld model (1916) represented a crucial extension of Bohr's atomic theory by incorporating relativistic effects and elliptical orbits through Wilson-Sommerfeld quantization rules.

Orbital Extensions

Rather than restricting electrons to circular orbits, Sommerfeld introduced elliptical orbits characterized by their semi-major axis a, semi-minor axis b, and eccentricity $e = \sqrt{1 - \frac{b^2}{a^2}}$. This generalization required additional quantum numbers beyond Bohr's principal quantum number: the azimuthal quantum number l for angular momentum, the magnetic quantum number m for spatial orientation, and a relativistic quantum number nr for radial motion.

Quantization Rules

The cornerstone of the theory lies in the generalized Wilson-Sommerfeld quantization condition. For any periodic coordinate q_i and its conjugate momentum p_i:

$$\oint p_i dq_i = n_i h$$

This manifests specifically in two key forms:
Radial quantization:

$$\oint p_r dr = n_r h$$

Angular quantization:

$$\oint p_\phi d\phi = n_\phi h$$

Relativistic Energy Levels

The model produced a refined energy level formula incorporating relativistic effects:

$$E_{n,k} = -\frac{mc^2\alpha^2}{2n^2}\left[1 + \frac{\alpha^2}{n^2}\left(\frac{n}{k} - \frac{3}{4}\right)\right]$$

where   is the fine structure constant, m is electron mass, c is speed of light, and k = n - |j + 1/2| + 1/2.

The model successfully explained several phenomena that Bohr's original theory could not address, including the fine structure of spectral lines and basic aspects of the Zeeman effect. However, it still fell short of explaining the anomalous Zeeman effect, intensity rules, and electron spin. Despite these limitations, the Bohr-Sommerfeld model served

> as a vital bridge between early quantum theory and modern quantum mechanics, introducing fundamental concepts like phase space quantization that would prove essential to later developments.

So far the Bohr model can successfully describe the line spectra. However, since electrons are assumed to propagate at circular orbits, they are supposed to permanently irradiate electromagnetic waves. This gives rise to the questions why does the electron not emit radiation and therefore lose energy and collapse into the nucleus? Or why are atoms stable?

About the stability of atoms

The stability of atoms in their lowest energetic state can be explained on the basis of the uncertainty principle. If we assume a being the average radius of a hydrogen atom, we can state the orbit radius with the uncertainty

$$\Delta r \leq a,$$

since we know the electron has to be somewhere within the atom. As a consequence the radial component p_r of the electron's momentum becomes

$$\Delta p_r \geq \frac{\hbar}{a},$$

Because of that, the overall electron momentum has to be bigger than the uncertainty

$$p \geq \frac{\hbar}{a},$$

otherwise we would know the momentum with a smaller uncertainty than Δp_r. For the electron's average kinetic and potential energy it follows

$$E_{\text{kin}} = \frac{p^2}{2m} \geq \frac{\Delta p^2}{2m} \geq \frac{\hbar^2}{2ma^2}$$

and

$$E_{\text{pot}} = -\frac{e^2}{4\pi\varepsilon_0 a},$$

respectively. The total energy $E = E_{\text{kin}} + E_{\text{pot}}$ then is given through

$$E \geq \frac{\hbar^2}{2ma^2} - \frac{e^2}{4\pi\varepsilon_0 a}$$

The probability to find an electron at the radius $a_{\min}$ is highest when the energy is at a minimum, which occurs at $\mathrm{d}E/\mathrm{d}a = 0$. This leads us to

$$a_{\min} = \frac{4\pi\varepsilon_0\hbar^2}{me^2} = \frac{\varepsilon_0 h^2}{\pi me^2} = a_0.$$

As a consequence, there is a state of minimum energy with the lower limit

$$E_{\min} = -\frac{me^4}{8\varepsilon_0^2 h^2} = -Ry^*.$$

This result is in accord with observations from the Bohr model stating the energy of the lowest state in a hydrogen atom is $E = -Ry^*$. Because of this discussion, we can state there is a finite distance $a_{\min}$ from the nucleus associated with the lowest energetic state. Due to the uncertainty relation the kinetic energy increases more rapidly than the potential energy decreases, if the electron moves closer to the nucleus than $a_{\min}$.