Balmer Series

At a time, when it was not even known that the atom consists of a core and electrons, the Balmer lines in hydrogen spectra were one of the first observations that could not be explained by classical physics. In this experiment, these Balmer lines can be produced with a gas-discharge tube via diffraction on a lattice, and their wavelengths may be calculated.
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1.1 Preparatory questions

- Explain the experiment in your own words.
- How does lattice diffraction work?
- What happens when beams are focused through a lens at an oblique angle?

1.2 Theory

1.2.1 Discoveries in the 2nd half of the 19th century

Astronomers and physicists were already watching star spectra as well as absorption and emission spectra of different gaseous substances. To everyone’s surprise the spectra were not continuous but had dark absorption or bright emission lines (see figure 1.1). Simply stated, a spectrum is called continuous when a colour transitions into another without any gaps between them. The sun light broken by drops of water making a rainbow appears to be continuous (due to the bad resolution). In contrast to such continuous spectra, there are those that only consist of single lines precisely at certain colours. The pattern of these lines can be highly complicated (e.g. the so-called Fraunhofer spectrum of the sun) or relatively simple (as e.g. the hydrogen spectrum). The origin of these lines was unknown back then. They were a riddle. A few stars had spectra that were identical to the absorption spectra of hydrogen. Thus, in 1885, Balmer established an empirical formula to calculate the frequencies of these lines:

\[ v_m = R \left( \frac{1}{4} - \frac{1}{m^2} \right) \]
\[ \lambda_m = \frac{c}{v_m} \]  \hspace{1cm} (1.1)

where \( m \geq 3 \) and \( R \) is a constant (the Rydberg frequency). This formula describes a regular series of lines for \( m = 3, 4, \ldots \) at frequencies \( v_m \) (resp. the wavelengths \( \lambda_m \)) that is known as the Balmer series. They are commonly denoted as: \( H_\alpha \ (m = 3) \), \( H_\beta \ (m = 4) \), etc.

Figure 1.1: Recorded with the 60 cm Schmitt mirror of UniversitÄt Basel’s observatory in Metzerlen. The image shows the spectrum of α Lyrae (Vega, in the Leier constellation). It consists of very intensive hydrogen absorption lines. The line on the far right is the \( H_\delta \) line. \( H_\alpha, \beta, \gamma \) cannot be seen, because the spectrum breaks off abruptly on the right side (the sensitivity of the photoemulsion is limited).

1.2.2 Developments in the beginning of the 20th century

The photoeffect

With the photoeffect (explained by Einstein in 1905) it could be shown impressively that radiation energy is quantised and the following relation holds:

\[ E = h v \]  \hspace{1cm} (1.2)
Here, $h$ is Planck’s constant, $\nu$ is the frequency of radiation and $E$ is the energy of the light quantum, the photon. (The experiment setup for the photoeffect lies just to the left).

**Half classical treatment: Bohr’s atom model**

From a classical viewpoint, an electron in the electric field of a nucleus can move along tracks of arbitrary radii (more exactly: ellipses of arbitrary semi-axes). This track depends only on the kinetic energy of the electron. Analogous to a satellite that orbits the earth, an electron would go along the one track where the radially outbound centrifugal force balances the radially inbound attractive force (Coulomb force, force of gravity for the satellite, see figure 1.2).

![Figure 1.2](image)

Figure 1.2: In the graph, both forces acting on the electron (dashed lines) and their sum (drawn through line) are plotted. $F_Z$ is dependent on the velocity of the electron and there is just one point – thus one track radius $r_{stab}$ – for which the forces are in balance, i.e. their sum equals zero.

However, this model is problematic. From electrodynamics we know that accelerated charges radiate energy (the circular motion is an accelerated motion). From this follows that there would not be any stable atoms, because the constant energy drain would cause the electron to sooner or later fall into the nucleus, just like satellites eventually fall to earth since they lose energy due to friction from the rest atmosphere at their track altitude. A way out of this dilemma was indicated by Niels Bohr who formulated a series of postulates in 1913. From these postulates follow several rules for electron behaviour:

- The electrons travel along certain discrete tracks around the nucleus (i.e. not every arbitrary radius is allowed any longer).
- There is a ground state energy, i.e. there is a state of minimal energy. Although the electron is still in accelerated motion, it does no longer radiate energy and thus does no longer fall into the nucleus. The ground state is stable.
- Electrons that are in higher excited states can reach lower states through emission of a photon.

The energy levels of hydrogen-like atoms (atoms with arbitrary nuclear charge $Ze$ and one electron, e.g. $H$, $He^+$, $Li^{2+}$, etc.) can be described using Bohr’s postulates in the following way:

$$E_n = -\frac{1}{2}Ma^2c^2\frac{Z^2}{n^2} \quad \text{oder} \quad E_n = \frac{E_1}{n^2} \quad (1.3)$$
where

\[ M = \text{electron mass} \]
\[ c = \text{vacuum speed of light} \]
\[ n = 1, 2, 3, \ldots \]
\[ \alpha = \frac{e^2}{\hbar c} \text{fine structure constant} \]

\( E_1 (n = 1) \) is the ground state energy. For hydrogen \((Z = 1)\) it equals \(-13.6 \, eV\). The energy levels can be illustrated in a so-called term diagram (figure 1.3). The ground state energy is negative, since the energy \(E = E_1\) has to be expended to completely separate the electron from the nucleus, i.e. to ionize the atom.

\[
E_1 = \frac{-M c^2}{2} \quad n=1
\]

\[
E_2 = \frac{-M c^2}{2} \quad n=2
\]

\[
E_3 = \frac{-M c^2}{2} \quad n=3
\]

\[
E_\ldots = \frac{-M c^2}{2} \quad n=5000
\]

**Figure 1.3:** Term diagram; the horizontal lines signify the possible electron energies.

Instead of the term diagram, we can also look at Bohr’s tracks of the electron (figure 1.4), since the two representations are equivalent. The term diagram is abstract, Bohr’s radii are more intuitively accessible. However, most physical properties of an atom can only sensibly be depicted in a term diagram (e.g., how would you draw Bohr’s tracks for \(n = 5000\) and \(n = 1\) in the same figure?). The relationship between the radius of one of Bohr’s tracks and the corresponding \(n\) is \(r_n \sim n^2\).

**Figure 1.4:** Bohr’s atom model - the depicted electron sits in its first excited state \((n = 2)\).

Transitions can only happen between the individual levels or from one track to another. Figuratively speaking, when doing so, the electron jumps from one track to another and changes its energy just as abruptly (figures 1.5, 1.6). For the energy of any one of these transitions, the following holds:

\[
\Delta E = E_i - E_f \quad (1.4)
\]

\(E_i\) denotes the energy of the electron before the transition, \(E_f\) the one after. Let \(n\) be the quantum number of the initial state, \(m\) the one of the final state. Then \(\Delta E\) can be written as
(only for hydrogen, $Z = 1$):

$$
\Delta E = \left( -\frac{1}{2} \frac{M \alpha^2 c^2}{n^2} \right) - \left( -\frac{1}{2} \frac{M \alpha^2 c^2}{m^2} \right) = \frac{1}{2} M \alpha^2 c^2 \left( \frac{1}{n^2} - \frac{1}{m^2} \right)
$$

(1.5)

(1.6)

If the initial state is of higher energy than the final state ($n > m$), the term ($\frac{1}{n^2} - \frac{1}{m^2}$) becomes negative in the above expression, thus $\Delta E$ becomes positive. Energy is released, i.e. such a transition can happen spontaneously by emitting a photon of energy $E_\nu = \Delta E = -\frac{1}{2} M \alpha^2 c^2 \left( \frac{1}{n^2} - \frac{1}{m^2} \right)$. Collectively, these transitions between all possible combinations of $n$ and $m$ (where $n > m$ always holds) is called emission spectrum and this is characteristic for a specific kind of atom or molecule (the lines created in this experiment represent the visible part of the hydrogen emission spectrum).

![Emission processes](image)

Figure 1.5: Emission processes; in a manner of speaking, the electron “falls” from a higher track to a lower one, releasing energy. From this energy, a photon is formed which is emitted (only 4 different possibilities are drawn in the term diagram, only one in the Bohr tracks, though actually there are infinitely many).

If the final state is of higher energy than the initial state ($m > n$), the term ($\frac{1}{n^2} - \frac{1}{m^2}$) becomes positive, thus $\Delta E$ becomes negative. To enable this transition, the electron must receive energy. In other words, the atom must be excited. This excitation can be accomplished by a photon. However, the energy of the photon must “fit” exactly, i.e. $E_\nu = \Delta E = \frac{1}{2} M \alpha^2 c^2 \left( \frac{1}{n^2} - \frac{1}{m^2} \right)$. This occurrence is called absorption. Irradiating a gas with white light (i.e. a mixture of all wavelengths) produces the likewise typical absorption spectra due to gas atoms or molecules only “swallowing” the respectively fitting photons. Figure 1.1 shows such an absorption spectrum. Note, that the lines tighten towards the left side (analogous to the energies within the term diagram). The absorption lines naturally lie at the same wavelengths as the emission lines. The Balmer formula thus gives the frequencies (or wavelengths) that enable absorption or emission in hydrogen (figure 1.7). Since it does not specify positive or negative energies, it is applicable to both processes. As described above, the lines for emission and absorption lie in the same position. They just represent respectively the inverse process.
Figure 1.6: Absorption processes; the photon can only be "swallowed" when its energy fits exactly \( E = \Delta E \). Then, the electron receives energy; it jumps to a higher track.

In the Balmer formula, there is only one variable \( m \); \( n \) is a constant and equals 2. Therefore, it is applicable either to emission processes with final state \( n = 2 \) (first excited state) or absorption processes from the already excited state \( n = 2 \). Additionally, the Rydberg frequency is given by:

\[
h\nu_m = \Delta E \implies hR \left( \frac{1}{4} - \frac{1}{m^2} \right) = \frac{1}{2} M\alpha^2 c^2 \left( \frac{1}{4} - \frac{1}{m^2} \right)
\]

\[
hR = \frac{1}{2} M\alpha^2 c^2
\]

\[
R = \frac{M\alpha^2 c^2}{2h}
\]

1.2.3 Spectral analysis with a lattice spectrometer

In order for constructive interference to happen, the path difference \( x \) must be an integral multiple of the wavelength (figure 1.8):

\[
a \sin(\theta) = n \lambda
\]

In the experiment described here, the screen shows the 0th \( (n = 0) \) and the 1st \( (n = 1) \) order interference. Depending on the light wavelength (three or four colours may be observed) the distance of the 1st order from the 0th order is different.
Figure 1.7: Transitions in the hydrogen spectrum.

Figure 1.8: Condition for interference with a lattice.
1.3 Experiment

1.3.1 Equipment

<table>
<thead>
<tr>
<th>Component</th>
<th>Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optical Bank</td>
<td>1</td>
</tr>
<tr>
<td>Balmer lamp</td>
<td>1</td>
</tr>
<tr>
<td>Lens ((f = 50mm))</td>
<td>1</td>
</tr>
<tr>
<td>Lens ((f = 100mm))</td>
<td>2</td>
</tr>
<tr>
<td>Aperture 1.5mm</td>
<td>1</td>
</tr>
<tr>
<td>Lattice with ca. 600 lines/mm</td>
<td>1</td>
</tr>
<tr>
<td>Transparent screen</td>
<td>1</td>
</tr>
<tr>
<td>UV glasses</td>
<td>2</td>
</tr>
</tbody>
</table>

1.3.2 Experimental setup and alignment

First, a few general guidelines for operating the Balmer lamp:

- The Balmer lamp is a gas-discharge tube filled with water vapour and runs on alternating current. The melted off tube is fed with water vapour from a water repository bound to a hygroscopic substrate. The water molecules are split into atomic hydrogen and a hydroxyl group through an electric discharge. A high temperature-resistant capillary within the lamp forces the discharge to a confined space, so a high concentration of atomic hydrogen is generated there. This atomic hydrogen is responsible for the intensive lines of the Balmer spectrum. An oxidized substance which is supported by suitable catalysts causes the hydrogen formed during the operation to be oxidized to water, s. t. a water cycle happens within the tube.

- For stable light of the Balmer lamp, a specific operation temperature is necessary (ca. 55°C, measured at the aluminium base). At too low temperature (directly after starting up) discharges may happen outside the capillary, which causes the lamp to flicker. Stable discharge conditions are reached after ca. 10 to 15 minutes.

- If the temperature of the lamp becomes too high (higher than ca. 70°C at the aluminium base), it might turn off after longer operation. In this case, it may be turned on again after it has cooled down.

- If, after longer operation time, the hot Balmer lamp does not fire when it is turned off and directly turned on again, you need to leave it off until it has cooled down again.

- Since the Balmer lamp also emits in the ultraviolet spectrum, UV-glasses need to be worn.

Next, build the following assembly on the optical bank:

1. Focus the light of the lamp with the lens \(L_1\) \((f = 50mm)\) on the aperture.
2. Using the lens \(L_2\) \((f = 100mm)\) create a parallel light beam that enters the lattice.
3. Lens \(L_3\) \((f = 100mm)\) is supposed to project the interference image sharply onto the screen.
4. Adjusting the lenses may further focus the lines on the screen.
1.3.3 Implementation and exercises for the analysis

1. While you set up the experiment, consider which distances between lenses, aperture and lattice you should choose. Why is the light of the lamp first focused on an aperture instead of directly on the lattice? In other words, what do you achieve by using the aperture and lenses $L_1$ and $L_2$?

2. The 0th and the 1st interference order are observable on the screen. Measure the distance of the 1st order from the 0th order. Use this to calculate the wavelengths of the different visible lines (wavelengths are usually expressed in $nm$ ($10^{-9}m$) or $Å$ ($10^{-10}m$)).

3. Calculate the theoretical wavelengths of the different lines with the Balmer formula (1.1) and compare them with your results ($R = 3.29 \cdot 10^{15} s^{-1}$).

4. Estimate the uncertainties of all measured variables in your measurement and do an uncertainty analysis.

5. Consider the influence of the fact that the focal plane of the final lens is actually not a plane, but a spherical surface. How could this effect be corrected?

6. As you can see in the term diagram (figure 1.3), the Balmer series is just one of the possible series of hydrogen. Why are you unable to see e. g. the Lyman or the Paschen series on the screen?
Wave-particle dualism and Bohr’s tracks

According to wave-particle dualism, the electron can be considered both as a wave and as a particle. Looking at the wave, it is now possible to explain the individual Bohr’s tracks. In 1924, deBroglie assigned a wavelength $\lambda$ to a particle with momentum $p$:

$$\lambda = \frac{h}{p} \quad (A.9)$$

For Bohr’s tracks the classical angular momentum gives on the one hand

$$L = mvr_n \quad (A.10)$$

On the other hand, Bohr’s postulates give the quantization of this angular momentum as

$$L = n\hbar \quad (A.11)$$

Using $p = mv$ gives

$$pr_n = nh \Rightarrow \frac{h}{\lambda}r_n = nh \Rightarrow \frac{h}{\lambda}r_n = n\frac{h}{2\pi} \Rightarrow 2\pi r_n = n\lambda \quad (A.12)$$

However, $2\pi r_n$ is exactly the length of the $n$th track which is thus an integral multiple of $\lambda$, according to the above calculation. So Bohr’s tracks are exactly those on which a stationary electron wave can be formed (figure A.10).
Figure A.10: The frequency spectrum of electromagnetic waves.