1.1.3: Quantization of Energy and Bohr Model of the Atom

Bohr's Atom Model

Rutherford's atom model was another big step forward in the development of atomic theory, however there were inherent problems with it as it violated fundamental principles of physics. An electron in an orbit is a self-accelerating electrically charged particle, and according to the laws of physics such particles must emit electromagnetic radiation. However, under normal circumstances atoms do not emit electromagnetic radiation. Secondly, even if the electron emitted electromagnetic radiation, then this would mean that the electron would lose energy because electromagnetic radiation is a form of energy. However, an electron constantly losing energy would make it unstable in its orbit around the nucleus, and it should spiral downward closer to the nucleus until the atom was eventually collapsed. It is however, experimentally not observed that atoms collapse, they are quite stable species. These difficulties of the Rutherford atom model meant that it could not be the final answer to atomic structure. Niels Bohr (Fig. 1.1.14) was aware of the problems of the Rutherford model, and two new developments in physics, namely the concept of the quantization of energy and atomic spectra helped him to develop an improved atom model, known as Bohr model. To understand this model let us look first at the quantization of energy and atomic spectra.

Figure 1.1.14 Niels Bohr (1885 - 1962) (Attribution: Bain News Service, publisher Restored by: Bammesk [Public domain], commons.wikimedia.org/wiki/F...in_-_35303.jpg)

Blackbody Radiation

The quantization of energy was discovered in the context of the physical phenomenon called "blackbody radiation". Blackbody radiation is the electromagnetic radiation any object sends out due to its temperature (Fig. 1.1.15).

Figure 1.1.15 An example of blackbody radiation emitted by hot, volcanic lava. (Attribution: Hawaii Volcano Observatory (DAS) [Public domain], commons.wikimedia.org/wiki/F...hoehoe_toe.jpg)

It's distribution of wavelengths follows curves that depend on the temperature and are shown in Figure 1.1.16. You can see that for each temperature the intensity first increases with increasing wavelength, then goes through a maximum, and finally decreases again. You can also see that the overall intensity of the blackbody radiation increases with temperature and that the maximum of the curve shifts to smaller wavelengths with increasing temperature. Objects at room temperature do not emit much blackbody radiation and the wavelengths are far longer than visible for the human eye. However, when an object is heated high enough, intensity increases and wavelength decreases, and the object starts to glow. For instance, lava (Figure 1.1.15) has a temperature high enough so that its blackbody radiation is visible for the human eye. With increasing temperature objects first glow red, then orange, then yellow, and eventually white. This is because red is the color associated with the largest wavelength, and as temperature increases other colors mix into red, until the object glows white. At extremely high temperatures the blackbody radiation also has a significant intensity in the UV region. Such temperatures occur in welding processes, for example, and for this reason welders need to wear glasses that block the UV radiation. The wavelength and intensity of blackbody radiation can be easily measured, but at the beginning of the 20th century there was no good explanation for its behavior. Classical theory predicted that intensity would continuously increase with decreasing wavelength at any temperature which was not in accordance with experimental observation.

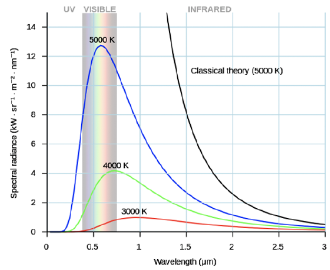

Figure 1.1.16 Experimentally measured intensity of blackbody radiation as a function of wavelength for 3000, 4000, and 5000 K vs. intensity predicted by classical theory (5000 K). (Attribution: Darth Kule commons.wikimedia.org/wiki/F...Black_body.svg)

To bring experiment and theory in accordance, Max Planck made the radical assumption that the energy associated with radiation of a given wavelength or a given frequency was quantized. It would be an integer multiple n of that frequency ν, multiplied with proportionality constant h, know today as the Planck constant.

$$E = n\,h\,\nu$$

Equation 1.1.1 The Planck-Einstein equation.

Using this assumption he was able to derive the Planck equation (Equation 1.1.2) which correctly describes the intensity and wavelength distribution of the blackbody radiation for any temperature. The correct description of blackbody radiation strongly supported Planck’s assumption that energy was quantized, but it did not prove it or explain it. The proof and the explanation was found only later. Initially Planck assumed it merely to fit the data.

$$E(\lambda, T) = \frac{2hc^2}{\lambda^5} * \frac{1}{e^{\left(\frac{hc}{\lambda kT}\right)} - 1}$$

$$\begin{aligned}
&\mathrm{h} = \text{Planck's constant} = 6.626 * 10^{-34}\ J * s \\
&\mathrm{c} = \text{speed of light} = 2.997925 * 10^{8}\ m\ /\ sec \\
&\lambda = \text{wavelength (m)} \\
&\mathrm{k} = \text{Boltzmann's constant} = 1.381 * 10^{-23}\ J/K \\
&\mathrm{T} = \text{temperature (K)}
\end{aligned}$$

Equation 1.1.2 Planck's equation

Bohr's Atom Model

The second development that contributed to Bohr’s atom model was the absorption and emission spectra of atoms. It was experimentally observed that under certain circumstances atoms would send out or absorb electromagnetic radiation of discreet wavelengths that were characteristic for an atom. For example, H atoms would absorb or emit at four discreet wavelengths in the visible region of the electromagnetic spectrum (Fig. 1.1.17).

Figure 1.1.17 The hydrogen emission spectrum in the visible region (Balmer series). (Attribution: Merikanto, Adrignola [CC0], commons.wikimedia.org/wiki/F...spectrum-H.svg)

This is known as the Balmer series named after its discoverer Johann Balmer. Friedrich Paschen and Chester Lyman later found that H also absorbs and emits at discreet wavelengths in the IR and UV region respectively. These wavelengths are known as the Paschen and Lyman series, respectively (Fig. 1.1.18).

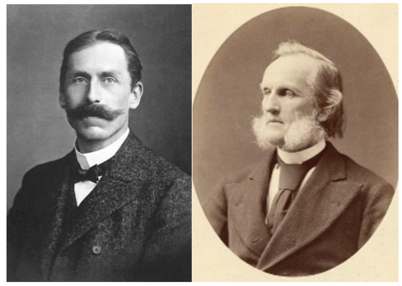

Figure 1.1.18 Friedrich Paschen (1865 – 1947) (Attribution: www.maerkischeallgemeine.de [Public domain], commons.wikimedia.org/wiki/F...n_Physiker.jpg) and Chester Lyman (1814-1988) (Attribution: commons.wikimedia.org/wiki/F...mith_Lyman.jpg), respectively.

For the absorption and emission spectra of H a simple mathematical relationship between the energies associated with the wavelengths can be found. The energy is proportional to a constant, today known as the Rydberg constant, times one over an integer number square minus one over another integer number square, whereby the second integer number would be larger than the first one (Eq. 1.1.3). The observation of integer numbers showed that also the energy and the wavelengths of the atomic absorption and emission spectra are quantized. The question was what the quantization of the absorption spectra meant for atomic structure.

$$\Delta E = R_H \left(\frac{1}{n_{low}^2} - \frac{1}{n_{high}^2} \right)$$

Equation 1.1.3 Rydberg formula for the emission of light with particular energies.

Bohr answered the question the following way. He argued, that like in the Rutherford model the electrons would move in orbits around the nucleus. A balance of opposite centrifugal forces and Coulomb attractions would hold the electron stable in the orbit. However, because energy is quantized, also the angular momentum of the electron would be quantized, and thus, only discreet radii would be allowed. The most inner orbit would have the quantum number n=1, the next higher orbit the quantum number n=2, and so forth (Fig. 1.1.19).

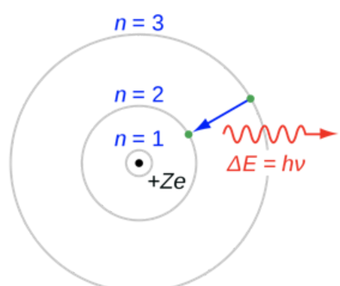

Figure 1.1.19 Bohr atom model (Attribution: JabberWok [CC BY-SA (http://creativecommons.org/licenses/by-sa/3.0/)], commons.wikimedia.org/wiki/F...atom_model.svg)

The quantization of the electron energies and the radii would be the explanation why electrons, despite self-accelerating, do not continuously emit electromagnetic radiation. Electromagnetic radiation is only emitted when an electron jumps from an outer orbit of higher energy to an inner orbit of lower energy. This radiation must have a discreet wavelength because the energy difference between two orbits is discreet. Vice versa, an atom can adsorb electromagnetic radiation of specific wavelength and energy that is suitable to make the electron jump from an inner to an outer orbit. In sum, the quantization of the energy and the radii would explain the quantization of the absorption and emission spectra. The question is: Can the radii be calculated, and what are the associated energies of the electrons in the orbits?

Bohr's Postulates (1913)

1. An electron in an atom moves in a circular orbit about the nucleus under the influence of the Coulomb attraction between the electron and the nucleus, obeying the laws of classical mechanics.

2. Instead of the infinity of orbits which would be possible in classical mechanics, it is only possible for an electron to move in an orbit for which its orbital angular momentum L is an integral multiple of h/2π.

3. Despite the fact that it is constantly accelerating, an electron moving in such an allowed orbit does not radiate electromagnetic energy. Thus, its total energy E remains constant.

4. Electromagnetic radiation is emitted if an electron, initially moving in an orbit of total energy, discontinuously changes its motion so that it moves in an other orbit of total energy. The frequency of the emitted radiation is equal to the quantity divided by h.

To calculate the radii and energies of the electron in the H atom Bohr made two assumptions: Firstly, the centrifugal force associated with the electron moving in the orbit would be assumed equal to the Coulomb force between the electron and the proton so that the electron would be stable in the orbit. Secondly, the angular momentum of the electron would be quantized and an integer multiple of the Planck constant h. The factor 2π is because E = h/2π x angular frequency. The angular frequency (also called angular speed) is the angular displacement (in degree or rad) per time unit. Angular frequency is frequency x 2π. We can rearrange this equation by solving it for *v* and then insert the equation into equation I giving the result as shown in Fig. 1.1.20.

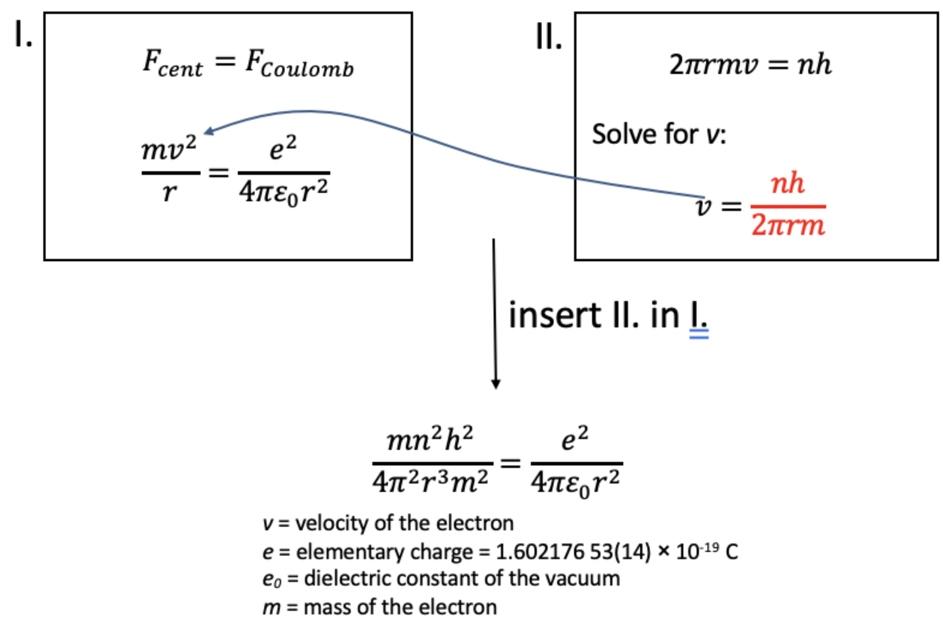

Figure 1.1.20 Derivation of the radii of the electron orbits (part 1).

We can then multiply this equation by $4\pi\varepsilon_0 r^2$, divide by e^2, and multiply it by r. This gives us the term $r=(n^2h^2\varepsilon_0)/(\pi me^2)$. Analyzing the term shows us that r is only a function of the quantum number n, specifically the radius is proportional to n^2 (Fig. 1.1.21). All other terms are constants, namely the Planck constant h, the dielectric constant of the vacuum, π, the mass of the electron, and the elementary charge. By inserting the quantum numbers into the equation we can calculate the actual values for the radii. For example, when we insert 1 for the quantum number n, we get the radius for the most inner orbit of the electron in the H atom. It is 5.29 x 10^{-11} m. If we inserted 2 for n, we would get the second radius, if we inserted 3, we would get the third radius and so on.

$$\frac{mn^2h^2}{4\pi^2r^3m^2} = \frac{e^2}{4\pi\varepsilon_0 r^2} \quad |\times 4\pi\varepsilon_0 r^2$$

$$\frac{n^2h^2\varepsilon_0}{\pi rm} = e^2 \quad | \div e^2 \quad |\times r$$

$$r = \frac{n^2h^2\varepsilon_0}{\pi me^2}$$

For the first radius (n=1): $$r = \frac{1^2h^2\varepsilon_0}{\pi me^2} = 5.29\times10^{-11}m$$

Figure 1.1.21 Continuation of the derivation of the radii of the electron orbits.

Now let us calculate the energies of the electron on these radii. Generally, the overall energy of the electron is the sum of the kinetic and potential energies. The kinetic energy of a moving object is given by $E_{kin}=1/2\ mv^2$. We know that m must be the mass of the electron, but what is the velocity of the electron? We can derive it from equation I we previously used by solving it for v^2 (Fig. 1.1.20). We can then insert the term for v^2 into the equation $E_{kin}=1/2\ mv^2$, which gives $E_{kin}=e^2/(8\pi\varepsilon_0 r)$, Fig. 1.1.23.

Now let us consider the potential energy. The potential energy is the Coulomb energy between the proton and the electron in the H atom. The formula for the Coulomb energy of two particles having two opposite elementary charges is $E_{pot}=-e^2/(4\pi\varepsilon_0 r)$. Note that this energy has a negative algebraic sign because the forces between the proton and the electron are attractive (Fig. 1.1.23).

$$E = E_{kin} + E_{pot}$$

$$E_{kin} = {}^1/_2\, mv^2 \qquad E_{pot} = -\frac{e^2}{4\pi\varepsilon_0 r}$$

Equation I: $$\frac{mv^2}{r} = \frac{e^2}{4\pi\varepsilon_0 r^2}$$

$$v^2 = \frac{e^2}{4\pi\varepsilon_0 rm}$$

$$E_{kin} = \frac{e^2}{8\pi\varepsilon_0 r}$$

Figure 1.1.23 Derivation of kinetic, potential, and overall energies of the H electron (part 1).

We can now add up the kinetic and the potential energy to give the overall energy which is $E = E_{kin}+E_{pot}= [e^2/(8\pi\varepsilon_0 r)] - [e^2/(4\pi\varepsilon_0 r)] = e^2/(\pi\varepsilon_0 r)\ (1/8-1/4) = -e^2/(8\pi\varepsilon_0 r)$. We can then use the term we previously calculated for r (Fig. 1.1.21) and insert it into the term for the overall energy. As a result the overall energy becomes $E=-(e^4m)/(8\varepsilon_0^2n^2h^2)$, Fig. 1.1.24. As we can see, the energies for the electrons in the different orbits are also only a function of the quantum number n, specifically, they are a function of $1/n^2$. Note also that the overall energy is negative. This is because the energy is a binding energy. Because of the negative algebraic sign, a higher quantum number n means a higher, because less negative energy. At very high quantum numbers n the value for E would approach zero, meaning that the binding energy for the electron would approach zero. The higher the orbit of the electron the more energy it has and the less strongly it is bound to the atom.

$$E = E_{kin} + E_{pot} = \frac{e^2}{8\pi\varepsilon_0 r} - \frac{e^2}{4\pi\varepsilon_0 r} = \frac{e^2}{\pi\varepsilon_0 r}\left(\frac{1}{8} - \frac{1}{4}\right) = -\frac{e^2}{8\pi\varepsilon_0 r}$$

B/c we had calculated before: $$r = \frac{n^2h^2\varepsilon_0}{\pi me^2} \longrightarrow E = -\frac{e^4m}{8\varepsilon_0^2n^2h^2}$$

Figure 1.1.24 Continued derivation for the energies of the H electron.

Formula for energy of electron in a specific orbit:

$$E = -\frac{e^4 m}{8\varepsilon_0^2 n^2 h^2}$$

Formula for energy difference between two orbits:

$$\Delta E = -\frac{e^4 m}{8\varepsilon_0^2 n_{high}^2 h^2} - -\frac{e^4 m}{8\varepsilon_0^2 n_{low}^2 h^2} = \frac{e^4 m}{8\varepsilon_0^2 h^2}\left(\frac{1}{n_{low}^2} - \frac{1}{n_{high}^2}\right)$$

Empirically Rydberg found the H spectrum:

$$\Delta E = R_H \left(\frac{1}{n_{low}^2} - \frac{1}{n_{high}^2}\right)$$

Because ΔE (theory) = ΔE (empirical):

$$R_H = \frac{e^4 m}{8\varepsilon_0^2 h^2}$$

Figure 1.1.25 Comparing derived energies of the H electron with those experimentally found in the H spectrum.

Finally let us calculate energy differences between electrons in different orbits. Subtraction of the terms for the energies of two electrons in two different orbits gives $\Delta E=(e^4m)/(8\varepsilon_0^2h^2)\ (1/(n_{low}^2\ ) - 1/(n_{high}^2\ ))$, Fig. 1.1.25. The calculated and empirically found ΔE match excellently, the empirically found Rydberg constant matches the theoretically derived constant $(e^4m)/(8\varepsilon_0^2h^2)$. Thus experiment and theory are in accordance. Bohr's theory is able to explain the H spectra very well, and can predict both radii of electron orbits and energies. The Bohr model for the first time introduced the quantization of electron states in atoms, and in this regard in was a big step forward. However, there were still problems with Bohr's theory. It could only explain the H spectra well, but failed to explain the spectra of all other atoms. Secondly, Bohr's postulates seemed ad hoc and lacked an explanation. There was no good explanation why an electron in a quantized orbit would not emit electromagnetic radiation continuously. Thus, the Bohr model could still not be the final answer to atomic theory. In fact, it lacks to take an important property of the electron into account: The wave-particle dualism of the electron.

Problems with Bohr's Theory

1. It can explain only the H spectrum and fails to explain all the spectra of all other atoms.
2. Bohr's postulates are ad hoc. They lack an explanation.

Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.