Abdelhafid Boussouf University Centre of Mila

Institute of Natural and Life Sciences,

Common Core Department

Abdelhafid Boussouf University Centre of Mila

General Chemistry

Course Support

CHAPTER III : BOHR'S ATOM

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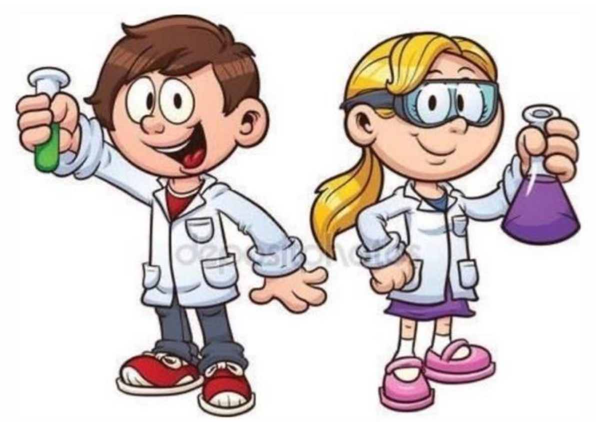

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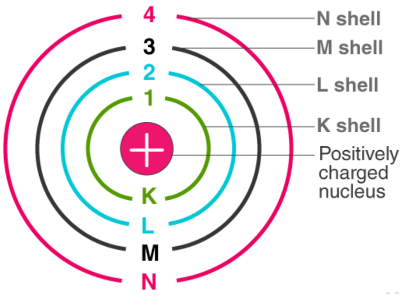
III.1 What is Bohr's Model of an Atom?

The Bohr model of the atom was proposed by Neil Bohr in 1915. It came into existence with the modification of Rutherford's model of an atom. Rutherford's model introduced the nuclear model of an atom, in which he explained that a nucleus (positively charged) is surrounded by negatively charged electrons.

III.2 Introduction to the Bohr Model

Bohr theory modified the atomic structure model by explaining that electrons move in fixed orbitals (shells) and not anywhere in between and he also explained that each orbit (shell) has a fixed energy. Rutherford explained the nucleus of an atom and Bohr modified that model into electrons and their energy levels.

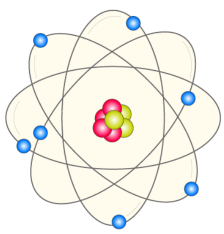


Bohr's Model of an Atom

Bohr's model consists of a small nucleus (positively charged) surrounded by negative electrons moving around the nucleus in orbits. Bohr found that an electron located away from the nucleus has more energy, and the electron which is closer to nucleus has less energy

III.3 Planetary Model of the Atom

Quantum mechanics emerged in the mid-1920s. Neil Bohr, one of the founders of quantum mechanics, was interested in the much-debated topic of the time – the structure of the atom. Numerous atomic models, including the theory postulated by J.J Thompson and the discovery of the nucleus by Ernest Rutherford, had emerged. But Bohr supported the planetary model, which asserted that electrons revolved around a positively charged nucleus just like the planets around the sun.



Historically, Bohr's model of the hydrogen atom is the very first model of atomic structure that correctly explained the radiation spectra of atomic hydrogen. The model has a special place in the history of physics because it introduced an early quantum theory, which brought about new developments in scientific thought and later culminated in the development of quantum mechanics. To understand the specifics of Bohr's model, we must first review the nineteenth-century discoveries that prompted its formulation.

When we use a prism to analyze white light coming from the sun, several dark lines in the solar spectrum are observed (**Figure 3.1**). Solar absorption lines are called **Fraunhofer lines** after Joseph von Fraunhofer, who accurately measured their wavelengths. During 1854–1861, Gustav Kirchhoff and Robert Bunsen discovered that for the various chemical elements, the line **emission spectrum** of an element exactly matches its line absorption spectrum. The difference between the **absorption spectrum** and the emission spectrum is explained in **Figure 3.2.** An absorption spectrum is observed when light passes through a gas. This spectrum appears as black lines that occur only at certain wavelengths on the background of the continuous spectrum of white light (**Figure 3.1**). The missing wavelengths tell us which wavelengths of the radiation are absorbed by the gas. The emission spectrum is observed when light is emitted by a gas. This spectrum is seen as colorful lines on the black background (see **Figure 3.3** and **Figure 3.4**). Positions of the emission lines tell us which wavelengths of the radiation are emitted by the gas. Each chemical element has its own characteristic emission spectrum. For each element, the positions of its emission lines are exactly the same as the positions of its absorption lines. This means that atoms of a specific element absorb radiation only at specific wavelengths and radiation that does not have these wavelengths is not absorbed by the element at all. This also means that the radiation emitted by atoms of each element has exactly the same wavelengths as the radiation they absorb.

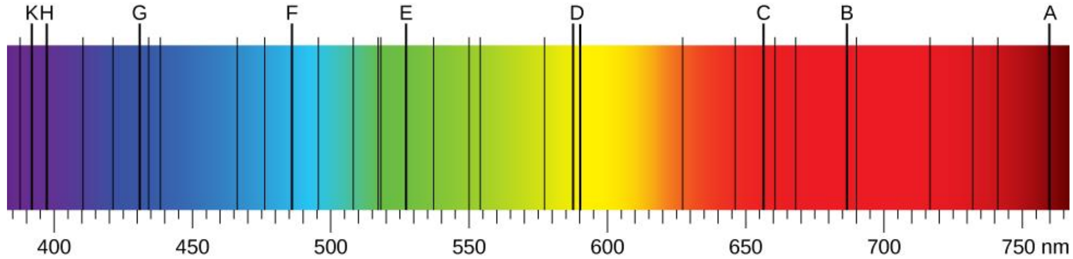


Figure 3.1 In the solar emission spectrum in the visible range from 380 nm to 710 nm, Fraunhofer lines are observed as vertical black lines at specific spectral positions in the continuous spectrum. Highly sensitive modern instruments observe thousands of such lines.

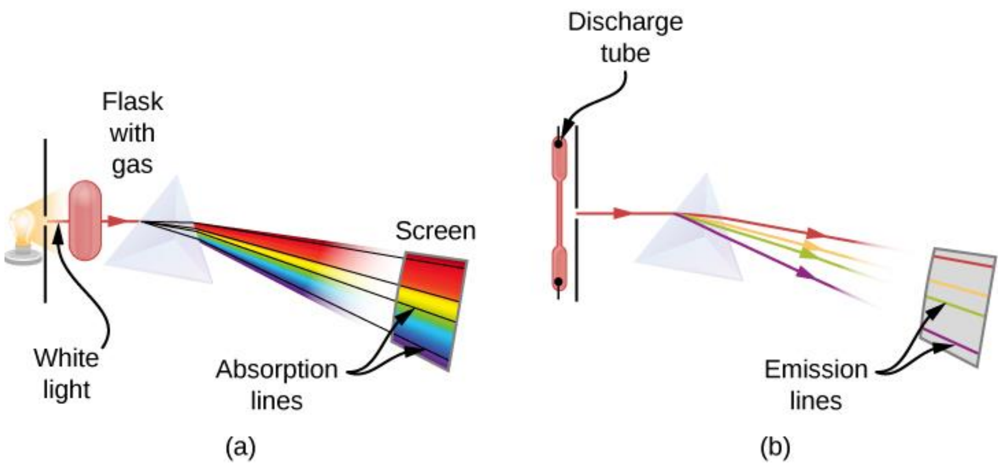


Figure 3.2 Observation of line spectra: (a) setup to observe absorption lines; (b) setup to observe emission lines. (a) White light passes through a cold gas that is contained in a glass flask. A prism is used to separate wavelengths of the passed light. In the spectrum of the passed light, some wavelengths are missing, which are seen as black absorption lines in the continuous spectrum on the viewing screen. (b) A gas is contained in a glass discharge tube that has electrodes at its ends. At a high potential difference between the electrodes, the gas glows and the light emitted from the gas passes through the prism that separates its wavelengths. In the spectrum of the emitted light, only specific wavelengths are present, which are seen as colorful emission lines on the screen.

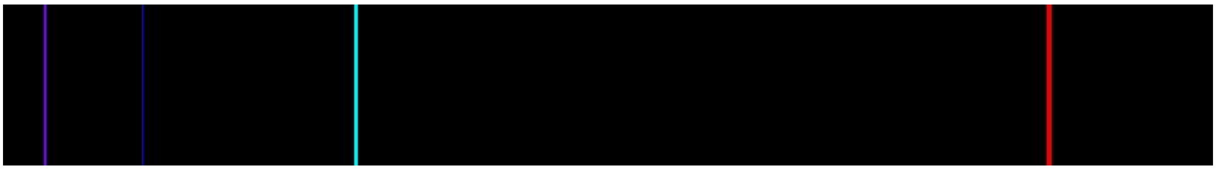


Figure 3.3 The emission spectrum of atomic hydrogen: The spectral positions of emission lines are characteristic for hydrogen atoms. (credit: “Merikanto”/Wikimedia Commons)

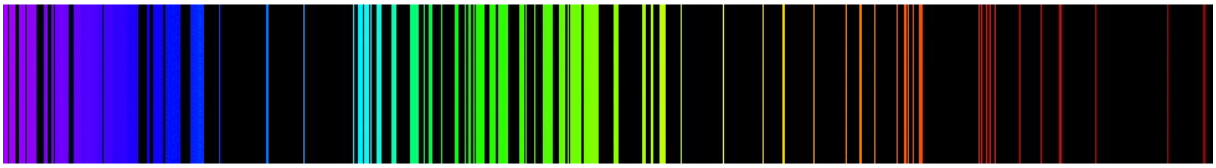


Figure 3.4 The emission spectrum of atomic iron: The spectral positions of emission lines are characteristic for iron atoms.

By observing the spectra from starlight and applying additional knowledge and calculations, astronomers can determine the makeup of objects millions of light-years away. In the 1920s, Cecilia Payne-Gaposchkin undertook a thorough analysis of a collection of stellar spectra that had been organized by astronomer Annie Jump Cannon. Up until that point, many researchers believed that stars — particularly the sun — were made up of similar elements to Earth, based in part on the spectral analysis. But Payne-Gaposchkin knew that Indian physicist Meghnad Saha had developed a method to calculate stellar ionization to obtain an accurate measure of star temperatures. After applying the Saha equation to the data at hand, Payne-Gaposchkin published a monumental paper demonstrating that stars were mostly made of hydrogen and helium, and that hydrogen was the most abundant element in the universe. Initially rejected, her work was soon proven to be true.

Emission spectra of the elements have complex structures; they become even more complex for elements with higher atomic numbers. The simplest spectrum, shown in Figure **3.3**, belongs to the hydrogen atom. Only four lines are visible to the human eye. As you read from right to left in Figure **3.3**, these lines are: red (656 nm), called the H- α line; aqua (486 nm), blue (434 nm), and violet (410 nm). The lines with wavelengths shorter than 400 nm appear in the ultraviolet part of the spectrum (Figure **3.3**, far left) and are invisible to the human eye. There are infinitely many invisible spectral lines in the series for hydrogen.

An empirical formula to describe the positions (wavelengths) λ of the hydrogen emission lines in this series was discovered in 1885 by Johann Balmer. It is known as the **Balmer formula:**

$$\frac{1}{\lambda} = R_{\mathrm{H}}\left(\frac{1}{2^2} - \frac{1}{n^2}\right).$$

The constant $RH=1.09737\times10^{7}m^{-1}$ is called the **Rydberg constant for hydrogen**. In Equation **6.31**, the positive integer n takes on values n=**3,4,5,6** for the four visible lines in this series. The series of emission lines given by the **Balmer formula** is called the Balmer series for hydrogen. Other emission lines of hydrogen that were discovered in the twentieth century are described by the **Rydberg formula**, which summarizes all of the experimental data:

$$\frac{1}{\lambda} = R_{\mathrm{H}}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right), \text{ where } n_i = n_f + 1, n_f + 2, n_f + 3, \ldots \tag{0}$$

When **nf=1**, the series of spectral lines is called the **Lyman series**. When **nf=2**, the series is called the **Balmer series**, and in this case, the Rydberg formula coincides with the Balmer formula. When **nf=3**, the series is called the **Paschen series**. When **nf=4**, the series is called the **Brackett series**. When **nf=5**, the series is called the **Pfund series**. As you may guess, there are infinitely many such spectral bands in the spectrum of hydrogen because **nf** can be any positive integer number.

The Rydberg formula for hydrogen gives the exact positions of the spectral lines as they are observed in a laboratory; however, at the beginning of the twentieth century, nobody could explain why it worked so well. The Rydberg formula remained unexplained until the first successful model of the hydrogen atom was proposed in 1913.

EXAMPLE

Limits of the Balmer Series

Calculate the longest and the shortest wavelengths in the Balmer series.

Strategy

We can use either the Balmer formula or the Rydberg formula. The longest wavelength is obtained when 1/ni is largest, which is when ni=nf+1=3, because nf=2 for the Balmer series. The smallest wavelength is obtained when 1/ni is smallest, which is 1/ni→0 when ni→∞.

Solution

The long-wave limit:

$$\frac{1}{\lambda} = R_{\mathrm{H}}\left(\frac{1}{2^2} - \frac{1}{3^2}\right) = (1.09737 \times 10^7)\frac{1}{\mathrm{m}}\left(\frac{1}{4} - \frac{1}{9}\right) \Rightarrow \lambda = 656.3\ \mathrm{nm}$$

The short-wave limit:

$$\frac{1}{\lambda} = R_{\mathrm{H}}\left(\frac{1}{2^2} - 0\right) = (1.09737 \times 10^7)\frac{1}{\mathrm{m}}\left(\frac{1}{4}\right) \Rightarrow \lambda = 364.6\ \mathrm{nm}$$

III.4 Postulates of Bohr's Model of an Atom

Bohr proposed the following three postulates of Bohr's model:

1- The negative electron moves around the positive nucleus (proton) in a circular orbit. All electron orbits are centered at the nucleus. Not all classically possible orbits are available to an electron bound to the nucleus.

2- The allowed electron orbits satisfy the first quantization condition: In the nth orbit, the angular momentum ***Ln*** of the electron can take only discrete values:

$$L_n = n\hbar, \text{ where } n = 1, 2, 3, \ldots \qquad (1)$$

This postulate says that the electron's angular momentum is quantized. Denoted by r_n and v_n, respectively, the radius of the nth orbit and the electron's speed in it, the first quantization condition can be expressed explicitly as

$$m_e v_n r_n = n\hbar. \qquad (2)$$

3- An electron is allowed to make transitions from one orbit where its energy is E_n to another orbit where its energy is E_m. When an atom absorbs a photon, the electron makes a transition to a higher-energy orbit. When an atom emits a photon, the electron transits to a lower-energy orbit. Electron transitions with the simultaneous photon absorption or photon emission take place instantaneously. The allowed electron transitions satisfy the second quantization condition:

$$hf = |E_n - E_m| \qquad (3)$$

where hf is the energy of either an emitted or an absorbed photon with frequency f. The second quantization condition states that an electron's change in energy in the hydrogen atom is quantized.

These three postulates of the early quantum theory of the hydrogen atom allow us to derive not only the Rydberg formula, but also the value of the Rydberg constant and other important properties of the hydrogen atom such as its energy levels, its ionization energy, and the sizes of electron orbits. Note that in Bohr's model, along with two nonclassical quantization postulates, we also have the classical description of the electron as a particle that is subjected to the Coulomb force, and its motion must obey Newton's laws of motion. The hydrogen atom, as an isolated system, must obey the laws of conservation of energy and momentum in the way we know from classical physics. Having this theoretical framework in mind, we are ready to proceed with our analysis.

III.5 Electron Orbits

To obtain the size rn of the electron's nth orbit and the electron's speed v_n in it, we turn to Newtonian mechanics. As a charged particle, the electron experiences an electrostatic pull toward the positively charged nucleus in the center of its circular orbit. This electrostatic pull is the centripetal force that causes the electron to move in a circle around the nucleus. Therefore, the magnitude of centripetal force is identified with the magnitude of the electrostatic force:

$$\frac{m_e v_n^2}{r_n} = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r_n^2}. \qquad (4)$$

Here, e denotes the value of the elementary charge. The negative electron and positive proton have the same value of charge,

$$|q|=e.$$

When **Equation 4** is combined with the first quantization condition given by **Equation 2**, we can solve for the speed, v_n, and for the radius, r_n:

$$v_n = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{\hbar}\frac{1}{n} \tag{5}$$

$$r_n = 4\pi\varepsilon_0\frac{\hbar^2}{m_e e^2}n^2. \tag{6}$$

Note that these results tell us that the electron's speed as well as the radius of its orbit depend only on the index n that enumerates the orbit because all other quantities in the preceding equations are fundamental constants. We see from Equation 6.38 that the size of the orbit grows as the square of n. This means that the second orbit is four times as large as the first orbit, and the third orbit is nine times as large as the first orbit, and so on. We also see from **Equation 5** that the electron's speed in the orbit decreases as the orbit size increases. The electron's speed is largest in the first Bohr orbit, for $n=1$, which is the orbit closest to the nucleus. The radius of the first Bohr orbit is called the Bohr radius of hydrogen, denoted as a_0. Its value is obtained by setting $n=1$ in **Equation 6**:

$$a_0 = 4\pi\varepsilon_0\frac{\hbar^2}{m_e e^2} = 5.29 \times 10^{-11}\,\mathrm{m} = 0.529\,\text{Å}. \tag{7}$$

We can substitute a_0 in **Equation 6.38** to express the radius of the nth orbit in terms of a_0:

$$r_n = a_0 n^2. \tag{8}$$

This result means that the electron orbits in hydrogen atom are quantized because the orbital radius takes on only specific values of $a_0, 4a_0, 9a_0, 16a_0$... given by **Equation 8**, and no other values are allowed.

III.6 Electron Energies

The total energy En of an electron in the nth orbit is the sum of its kinetic energy K_n and its electrostatic potential energy U_n. Utilizing **Equation 5**, we find that

$$K_n = \frac{1}{2}m_e v_n^2 = \frac{1}{32\pi^2\varepsilon_0^2}\frac{m_e e^4}{\hbar^2}\frac{1}{n^2}. \tag{9}$$

Recall that the electrostatic potential energy of interaction between two charges q_1 and q_2 that are separated by a distance r_{12} is $(1/4\pi\varepsilon_0)\, q_1q_2/r_{12}$. Here, $q_1=+e$ is the charge of the nucleus in the hydrogen atom (the charge of the proton), $q_2=-e$ is the charge of the electron and $r_{12}=r_n$ is the radius of the ***nth*** orbit. Now we use **Equation 6** to find the potential energy of the electron:

$$U_n = -\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r_n} = -\frac{1}{16\pi^2\varepsilon_0^2}\frac{m_e e^4}{\hbar^2}\frac{1}{n^2}. \tag{10}$$

The total energy of the electron is the sum of **Equation 9** and **Equation 10**:

$$E_n = K_n + U_n = -\frac{1}{32\pi^2\varepsilon_0^2}\frac{m_e e^4}{\hbar^2}\frac{1}{n^2}. \tag{11}$$

Note that the energy depends only on the index n because the remaining symbols in **Equation 11** are physical constants. The value of the constant factor in **Equation 11** is

$$E_0 = \frac{1}{32\pi^2\varepsilon_0^2}\frac{m_e e^4}{\hbar^2} = \frac{1}{8\varepsilon_0^2}\frac{m_e e^4}{h^2} = 2.17 \times 10^{-18}\,\mathrm{J} = 13.6\,\mathrm{eV}. \tag{12}$$

It is convenient to express the electron's energy in the nth orbit in terms of this energy, as

$$E_n = -E_0\frac{1}{n^2}. \tag{13}$$

Now we can see that the electron energies in the hydrogen atom are quantized because they can have only discrete values of ***$-E_0$, $-E_0/4$, $-E_0/9$, $-E_0/16$***...given by **Equation 13,** and no other energy values are allowed. This set of allowed electron energies is called the energy spectrum of **hydrogen** (**Figure 3.5**). The index n that enumerates energy levels in Bohr's model is called the energy **quantum number**. We identify the energy of the electron inside the hydrogen atom with the energy of the hydrogen atom. Note that the smallest value of energy is obtained for n=1, so the hydrogen atom cannot have energy smaller than that. This smallest value of the electron energy in the hydrogen atom is called the **ground state energy of the hydrogen atom** and its value is

$$E_1 = -E_0 = -13.6\,\mathrm{eV}. \tag{14}$$

The hydrogen atom may have other energies that are higher than the ground state. These higher energy states are known as excited energy states of a hydrogen atom.

There is only one ground state, but there are infinitely many excited states because there are infinitely many values of n in **Equation 13**. We say that the electron is in the "first exited state" when its energy is **E_2** (when **n=2**), the second excited state when its energy is **E_3** (when **n=3**) and, in general, in the nth exited state when its energy is E_{n+1}**.** There is no highest-of-all excited state; however, there is a limit to the sequence of excited states. If we keep increasing ***n*** in **Equation 13**, we find that the limit is $-\lim_{n\to\infty} E_0/n^2 = 0$

In this limit, the electron is no longer bound to the nucleus but becomes a free electron. An electron remains bound in the hydrogen atom as long as its energy is negative. An electron that orbits the nucleus in the first Bohr orbit, closest to the nucleus, is in the ground state, where its energy has the smallest value. In the ground state, the electron is most strongly bound to the nucleus and its energy is given by **Equation 14**. If we want to remove this electron from the atom, we must supply it with enough energy, $\boldsymbol{E_\infty}$, to at least balance out its ground state energy E_1:

$$E_\infty + E_1 = 0 \Rightarrow E_\infty = -E_1 = -(-E_0) = E_0 = 13.6\,\text{eV}. \qquad (15)$$

The energy that is needed to remove the electron from the atom is called the ionization energy. The ionization energy $\boldsymbol{E_\infty}$ that is needed to remove the electron from the first Bohr orbit is called the ionization limit of the hydrogen atom. The ionization limit in **Equation 15** that we obtain in Bohr's model agrees with experimental value.

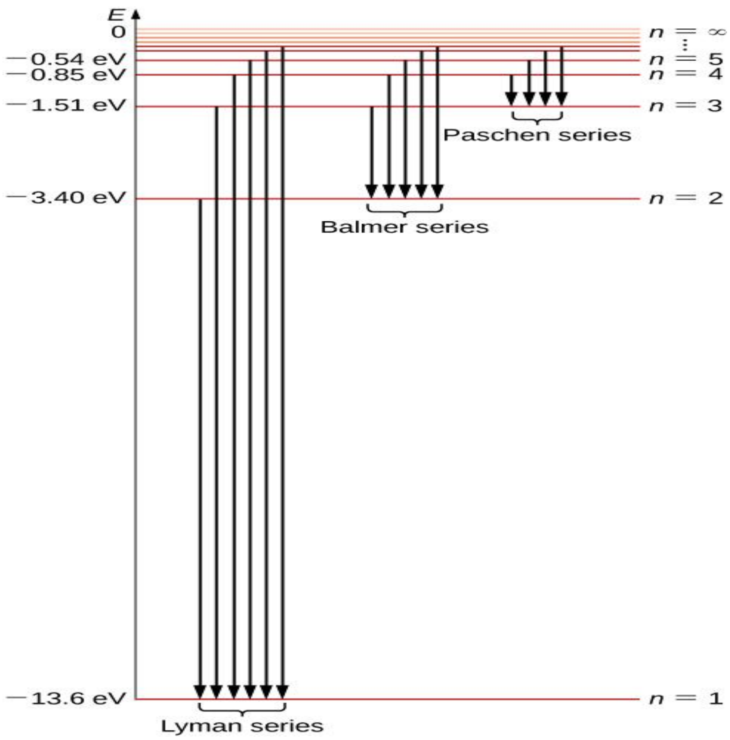


Figure 3.5 The energy spectrum of the hydrogen atom. Energy levels (horizontal lines) represent the bound states of an electron in the atom. There is only one ground state, n=1, and infinite quantized excited states. The states are enumerated by the quantum number **n=1,2,3, 4...**Vertical lines illustrate the allowed electron transitions between the states. Downward arrows illustrate transitions with an emission of a photon with a wavelength in the indicated spectral band.

III.7 Spectral Emission Lines of Hydrogen

To obtain the wavelengths of the emitted radiation when an electron makes a transition from the nth orbit to the *mth* orbit, we use the second of Bohr's quantization conditions and

Equation 13 for energies. The emission of energy from the atom can occur only when an electron makes a transition from an excited state to a lower-energy state. In the course of such a transition, the emitted photon carries away the difference of energies between the states involved in the transition. The transition cannot go in the other direction because the energy of a photon cannot be negative, which means that for emission we must have En>Em and n>m. Therefore, the third of Bohr's postulates gives

$$hf = \left|E_n - E_m\right| = E_n - E_m = -E_0\frac{1}{n^2} + E_0\frac{1}{m^2} = E_0\left(\frac{1}{m^2} - \frac{1}{n^2}\right). \qquad (16)$$

Now we express the photon's energy in terms of its wavelength, hf=hc/λ, and divide both sides of **Equation 16** by ***hc***. The result is

$$\frac{1}{\lambda} = \frac{E_0}{hc}\left(\frac{1}{m^2} - \frac{1}{n^2}\right). \qquad (17)$$

The value of the constant in this equation is

$$\frac{E_0}{hc} = \frac{13.6\,\mathrm{eV}}{(4.136\ \times\ 10^{-15}\mathrm{eV\cdot s})(2.997\ \times\ 10^{8}\mathrm{m/s})} = 1.097\ \times\ 10^{7}\frac{1}{\mathrm{m}}. \qquad (18)$$

This value is exactly the Rydberg constant R_H in the Rydberg heuristic formula Equation 0. In fact, Equation 17 is identical to the Rydberg formula, because for a given m, we have **n=m+1, m+2....** In this way, the Bohr quantum model of the hydrogen atom allows us to derive the experimental Rydberg constant from first principles and to express it in terms of fundamental constants. Transitions between the allowed electron orbits are illustrated in **Figure 3.5**.

We can repeat the same steps that led to Equation 17 to obtain the wavelength of the absorbed radiation; this again gives Equation 17 but this time for the positions of absorption lines in the absorption spectrum of hydrogen. The only difference is that for absorption, the quantum number m is the index of the orbit occupied by the electron before the transition (lower-energy orbit) and the quantum number n is the index of the orbit to which the electron makes the transition (higher-energy orbit). The difference between the electron energies in these two orbits is the energy of the absorbed photon.

Bohr's model of the hydrogen atom also correctly predicts the spectra of some hydrogen-like ions. Hydrogen-like ions are atoms of elements with an atomic number Z larger than one (Z=1 for hydrogen) but with all electrons removed except one. For example, an electrically neutral helium atom has an atomic number Z=2. This means it has two electrons orbiting the nucleus with a charge of q=+Ze. When one of the orbiting electrons is removed from the helium atom (we say, when the helium atom is singly ionized), what remains is a hydrogen-like atomic structure where the remaining electron orbits the nucleus with a charge of q=+Ze.

This type of situation is described by the Bohr model. Assuming that the charge of the nucleus is not +e but +Ze, we can repeat all steps, beginning with Equation 6.36, to obtain the results for a hydrogen-like ion:

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

where a_0 is the Bohr orbit of hydrogen, and

$$E_n = -Z^2 E_0 \frac{1}{n^2}$$

where E_0 is the ionization limit of a hydrogen atom. These equations are good approximations as long as the atomic number Z is not too large.

The Bohr model is important because it was the first model to postulate the quantization of electron orbits in atoms. Thus, it represents an early quantum theory that gave a start to developing modern quantum theory. It introduced the concept of a quantum number to describe atomic states. The limitation of the early quantum theory is that it cannot describe atoms in which the number of electrons orbiting the nucleus is larger than one. The Bohr model of hydrogen is a semi-classical model because it combines the classical concept of electron orbits with the new concept of quantization. The remarkable success of this model prompted many physicists to seek an explanation for why such a model should work at all, and to seek an understanding of the physics behind the postulates of early quantum theory. This search brought about the onset of an entirely new concept of "matter waves."

In an atom, electrons (negatively charged) revolve around the positively charged nucleus in a definite circular path called orbits or shells.

III.8 Limitations of Bohr's Model of an Atom

The Bohr Model was an important step in the development of atomic theory. However, it has several limitations.

- It is in violation of the Heisenberg Uncertainty Principle. The Bohr Model considers electrons to have both a known radius and orbit, which is impossible according to Heisenberg.
- The Bohr Model is very limited in terms of size. Poor spectral predictions are obtained when larger atoms are in question.
- It cannot predict the relative intensities of spectral lines.
- It does not explain the Zeeman Effect, when the spectral line is split into several components in the presence of a magnetic field.

- The Bohr Model does not account for the fact that accelerating electrons do not emit electromagnetic radiation.