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An Institute of NET-JRF, IIT-JAM, GATE, JEST, TIFR & CUET in Physics & Physical Sciences

Atomic & Molecular Physics

(NET/JRF, GATE, JEST, TIFR)

ATOMIC AND MOLECULAR PHYSICS
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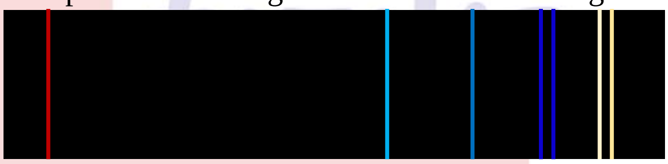
CHAPTER-1
ATOMIC SPECTRA AND BOHR MODEL OF HYDROGEN ATOM

1.1 Atomic Spectra

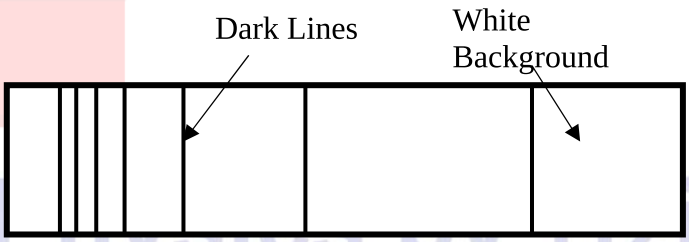
When atoms or molecules are exposed to the electromagnetic radiation, they may absorb photon of certain frequencies and reach to the higher quantum state. While returning to the normal or ground state, they emit radiations of different frequencies. Atoms gives discontinuous or line spectrum consisting of bright lines or bands separate from each other by a dark space. There are two types of atomic spectra.

i. Atomic Emission Spectra**:** When a sample of atomic vapours is suitably excited by either heating to high temperature or passing electric current through it, emit radiation of certain wavelength (or frequencies). These emitted radiation produces a spectrum consisting of bright lines in black background is known as atomic emission spectra. Each line in the emission spectrum corresponds to a specific wavelength and no two elements give the same.



ii. Atomic Absorption Spectra**:** When white light is passed through the same atomic gas, it absorbs light of certain wavelength present in the emission spectrum. The resulting spectrum consisting of dark lines on white background is known as absorption spectrum.

Dark line in the absorption spectrum and bright lines in the emission spectrum of the same elements appears at the same wavelength.



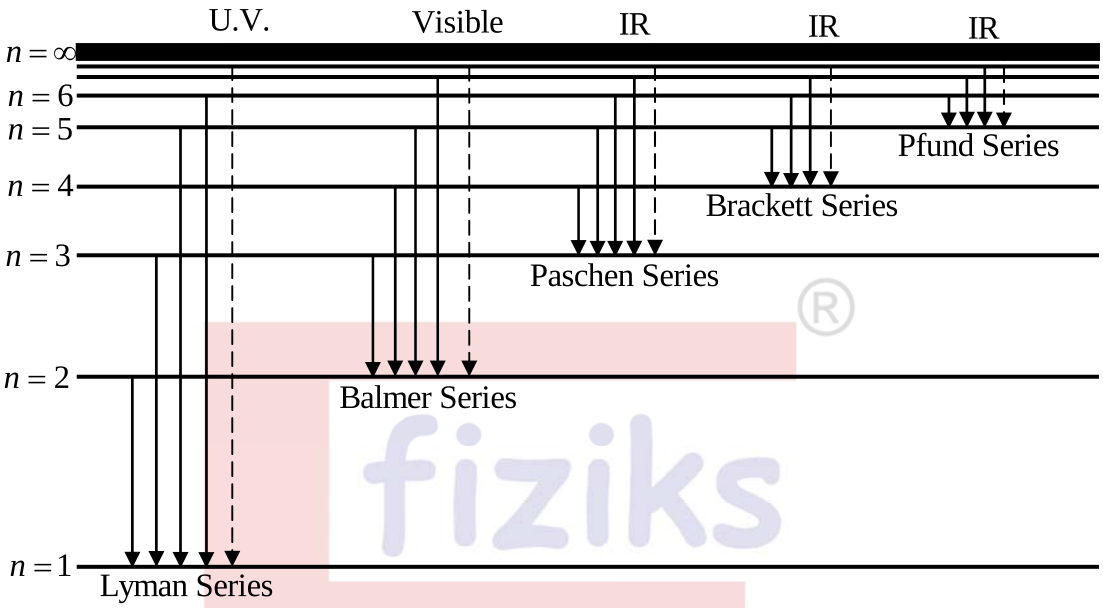
Since each element gives characteristics line spectrum, hence the atomic spectrum is used for element analysis.

1.2 Spectrum of Atomic Hydrogen

It has been discovered that when atoms exposed to white light can absorb light at certain discrete frequencies known as absorption lines or when atoms are excited by the passage of an electric current or by some another means produces discrete frequencies of light known as emission line. The spectrum of light absorbed or emitted by an element is carrying the signature of that element, e.g. Sodium burning in flame, produces two distinct yellow light of wavelength $5896\,\overset{o}{A}$ and $5890\,\overset{o}{A}$ which is observed after being dispersed by a suitable spectrometer. Each of the wavelength components is called a spectral line and whole family of lines is called a line spectrum. No two different elements can produce similar spectrum. The fact that each element produces its own characteristic spectrum, is of great importance as this information can be used for the chemical or element analysis, for example the elements present in Sun are analysed by this means. J. Balmer (1885) and J. Rydberg (1888) found that the spectral lines in hydrogen atom obey the following mathematical formula

$$\nu = \frac{1}{\lambda} = R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

Where v is the frequency of either an emission or absorption line, n_i and n_f are positive integer with $n_i > n_f$ and R is a constant, known as Rydberg's constant.



In atomic hydrogen, different line series are observed which are described below

1. *Lyman Series*: The series with $n_f = 1$ is known as the Lyman series and lies in the ultraviolet part of the spectrum. $\frac{1}{\lambda} = R\left(\frac{1}{1^2} - \frac{1}{n_i^2}\right)$ $\quad n_i = 2, 3, 4...$

The lines are labeled as L_α, L_β, L_γ ……… in order of decreasing wavelengths.

L_α line: $n_f = 1$ and $n_i = 2$; $\lambda = 1216\,\overset{o}{A}$

L_β line: $n_f = 1$ and $n_i = 3$; $\lambda = 1026\,\overset{o}{A}$

L_γ line: $n_f = 1$ and $n_i = 4$; $\lambda = 973\,\overset{o}{A}$

While the Lyman series limit ($n_i \to \infty$) is $\lambda = 912\,\overset{o}{A}$.

2. *Balmer Series*: Balmer series ($n_f = 2$) was first to be discovered and it lies in the visible part of electromagnetic spectrum. $\frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{n_i^2}\right)$ $\quad n_i = 3, 4, 5...$

The lines are labeled as H_α, H_β, H_γ ……… in order of decreasing wavelengths.

H_α line: $n_f = 2$ and $n_i = 3$; $\lambda = 6563\,\overset{o}{A}$

H_β line: $n_f = 2$ and $n_i = 4$; $\lambda = 4861\,\overset{o}{A}$

H_γ line: $n_f = 2$ and $n_i = 5$; $\lambda = 4340\,\overset{o}{A}$

While the Balmer series limit ($n_i \to \infty$) is $\lambda = 3646\,\overset{o}{A}$. The H_α is an important line used in the detection of hydrogen presence.

3. *Paschen Series*: Paschen series was observed by Friedrich Paschen in 1908 corresponds to the transition between the states with $(n_f = 3)$ and successive higher states and lies in the near Infrared region of the spectrum.

$$\frac{1}{\lambda} = R\left(\frac{1}{3^2} - \frac{1}{n_i^2}\right) \qquad n_i = 4, 5, 6...$$

The Paschen series starts with a line at $18751\,\mathring{A}$ and ends at $8204\,\mathring{A}$ (wavelength of Paschen series limit).

4. *Brackett Series*: In the Brackett series electron transition takes place from any higher principle quantum state to $n_f = 4$ and it is obtained in the far infrared region.

$$\frac{1}{\lambda} = R\left(\frac{1}{4^2} - \frac{1}{n_i^2}\right) \qquad n = 5, 6, 7.........$$

The Brackett series start at $40500\,\mathring{A}$ whereas the series limit lies at $14580\,\mathring{A}$. The shortest or high frequency lines of Brackett series overlap with the Paschen series lines.

5. *Pfund Series*: This series was discovered by A.H. Pfund in 1924 which corresponds to transition between the states with $(n_f = 5)$ and successive higher states and lies in Infrared region of the spectrum.

$$\frac{1}{\lambda} = R\left(\frac{1}{5^2} - \frac{1}{n_i^2}\right) \qquad n_i = 6, 7, 8.....$$

The Pfund series start at $74600\,\mathring{A}$ whereas the series limit lies at $22790\,\mathring{A}$.

6. *Humphreys Series*: The sixth series in the spectrum of hydrogen atom was observed by C.J. Humphreys in 1953 and lies in the infrared region of the spectrum. This series originates in transition to the sixth orbit from those of greater quantum numbers.

$$\frac{1}{\lambda} = R\left(\frac{1}{6^2} - \frac{1}{n_i^2}\right) \qquad n_i = 7, 8, 9.....$$

The series with higher orders is unnamed but it follows the same rule given by J. Rydberg formula.

1.3 Bohr Model of Hydrogen Atom

Bohr's Postulates

Bohr formulated three postulates which describe the deviations from classical behavior for the electrons in an atom. They are:

1. The classical equations of motion are valid for electrons in atoms. However, only certain discrete orbits with energies E_n are allowed. These are called the energy levels of the atoms.
2. The motion of electrons in these quantized orbits is radiation less. An electron can be transferred from an orbit of higher energy (lower negative binding energy) to an orbit with lower energy (higher negative binding energy) by emitting radiation. The frequency of radiation is given by

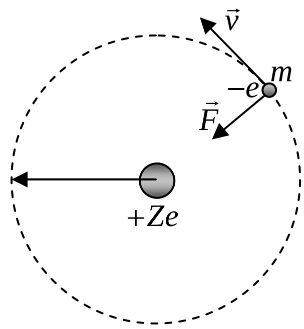
$$E_{n'} - E_n = h\upsilon, \text{ where } E_n = -\frac{Rhc}{n^2} \quad \text{and} \quad E_{n'} = -\frac{Rhc}{n'^2}$$

3. Out of the infinite number of orbits which would be possible in classical mechanics, it is only possible for an electron to move in an orbit for which the magnitude of its orbital angular momentum $\vec{l}$ is an integral multiple of $\frac{h}{2\pi}$, where h is Plank's constant.

$$\left|\vec{l}\right| = n\frac{h}{2\pi};\ n = 1, 2, 3...$$

This postulate introduces quantization. The quantization of the orbital angular momentum of the atomic electron leads to the quantization of its total energy.

Estimation of atomic radius



Bohr's determine the atomic energy states by considering an atom consisting of nucleus $+Ze$ and mass M, and single electron of charge –e and mass m. The condition of stable electronic orbital is

Coulomb force = Centripetal force

$\frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r^2} = \frac{m\text{v}^2}{r}$, where v is the electron speed and r is the orbital radius.

The orbital angular momentum of electron, $L = m\text{v}r$, must be a constant, because the force acting on the electron is entirely in the radial direction. Applying the quantization condition $L = n\hbar$, (where n = 1,2,3,4,5 …..).

$$m\text{v}r_n = n\hbar \Rightarrow \text{v} = \frac{n\hbar}{mr_n} \Rightarrow \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r_n^2} = \frac{mn^2\hbar^2}{m^2r_n^3}$$

we get the expression of velocity and radius.

Radius: $r_n = 4\pi\epsilon_0\frac{n^2\hbar^2}{mZe^2} = a_0\frac{n^2}{Z}$, where, $a_0 =$ Bohr radius $= 0.52A^0$

Velocity: $\text{v}_n = \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{n\hbar} = \alpha c$

where, α is the fine structure constant defined as

$$\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} \approx \frac{1}{137}$$

Estimation of total energy

The total energy of the atom, which contain both kinetic energy and potential energy term is,

$$E = K + V = \frac{1}{2}m\text{v}_n^2 - \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r_n}$$

Thus, the total energy of the electron

$$E = \frac{1}{2}\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r_n} - \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r_n} = -\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r_n}$$

Using equation of r_n we get,

$$E = -\frac{mZ^2e^4}{(4\pi\varepsilon_0)^2 2\hbar^2}\frac{1}{n^2} = -\frac{me^4}{8\varepsilon_0^2h^2}\frac{Z^2}{n^2} = E_1\frac{Z^2}{n^2}$$

This shows that, quantization of the orbital angular momentum of the electron leads to a quantization of its total energy.

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Energy levels for Hydrogen atom **($Z = 1$):**

$$E_n = -\frac{me^4}{8\varepsilon_0^2 h^2}\frac{1}{n^2} = \frac{E_1}{n^2}, \qquad n = 1, 2, 3, ...$$

where $E_1 = -\frac{me^4}{8\varepsilon_0^2 h^2} = -13.6\ eV$

Thus, the energy of the hydrogen atom is

Energy: $$E_n = -\frac{13.6}{n^2} eV$$

The total energy of the electron is negative. This holds for every atomic electron and reflects the fact that it is bound to the nucleus. An atomic electron can have only these energies and no others. The integer n corresponds to the discrete or quantized atomic energy levels and named as principle quantum number.

The lowest energy level E_1 is called the **ground state** of the atom, and the higher levels E_2, E_3, E_4, . . . are called **excited states.** As the quantum number n increases, the corresponding energy E_n approaches closer to 0. In the limit of $n = \infty$, $E_n = 0$ and the electron is no longer bound to the nucleus to form an atom.

Origin of line spectrum

Line spectrum arises when electron jump from one level to another level, with a difference in energy between the levels appears as a single photon.

The minimum energy required to ionize the atom (that is, to completely remove an electron in the ground state from the proton's influence) is called the ionization energy.

If the quantum number of the initial (higher energy) state is n_i and the quantum number of the final (lower-energy) state is n_f, we are asserting that

Initial energy – Final energy = Photon energy

$$E_i - E_f = h\upsilon$$

Substituting the E_i and E_f, we have

$$E_i - E_f = E_1\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) = -E_1\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

The frequency of the emitted photon υ is

$$\upsilon = \frac{E_i - E_f}{h} = -\frac{E_1}{h}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

Because the quantity actually measured is wavelength, it is convenient to convert frequency to wavelength using $c = \upsilon\lambda$ to get

$$\frac{1}{\lambda} = -\frac{E_1}{ch}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) = R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

where R is the Rydberg constant

$$R = -\frac{E_1}{ch} = 1.097 \times 10^7 m^{-1}$$

Above equation states that the radiation emitted by excited hydrogen atoms should contain certain wavelengths only. These wavelengths, furthermore, fall into definite sequences that depend upon the quantum number n_f of the final energy level of the electron.

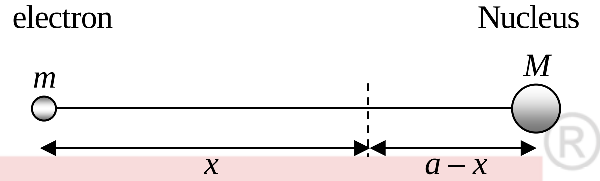
Since $n_i > n_f$ in each case, in order that there be an excess of energy to be given off as a photon, the calculated formulas for the first six series are already shown in section 1.2.

Bohr's Correspondence Principle

According to classical theory, an oscillating charged system would emit radiation of a particular frequency, namely, the frequency of oscillation itself.

For example, an electron moving in a circular orbit radiates em waves whose frequencies are equal to its frequency of revolution.

In hydrogen atom the speed of the electron is $v = \frac{e}{\sqrt{4\pi m r}}$



Hence the frequency of revolution f of the electron is

$$f = \frac{\text{Electron speed}}{\text{orbital circumference}} = \frac{v}{2\pi r} = \frac{e}{2\pi\sqrt{4\pi m r^3}}$$

The radius r of a stable orbit is given by $r = \frac{n^2 h^2 \varepsilon_0}{\pi m e^2}$

and so the frequency of the revolution is $f = \frac{me^4}{8\varepsilon_0^2 h^3}\left(\frac{2}{n^3}\right)$

Energy expression when nuclear mass is included

In the Bohr theory, we have assumed that the nucleus of the H atom is so heavy that it remains fixed at the centre of the circular orbit, while the electron revolves round it. But this will be true only when the mass of the nucleus is infinitely large as compared with the case of the electron. In fact the nucleus has finite mass. The nucleus of H atom is about 1836 times as heavy as electron and hence the assumption that the nucleus is fixed is not justified. Therefore, the nucleus and the electron revolve round a common centre of mass with same angular velocity the nucleus in an orbit of smaller radius as compared to electron orbit.

Let us consider that the electron (m) and nucleus (M) revolve around their common center of mass O which remains fixed in space. In equilibrium, the moment of m and M about O will be equal.

$$mx = M(a-x) \Rightarrow x = \frac{Ma}{m+M} \text{ and } a - x = \frac{ma}{m+M}$$

The total angular momentum of the atom

$$L = mx^2\omega + M(a-x)^2\omega = m\frac{M^2a^2}{(m+M)^2}\omega + M\frac{m^2a^2}{(m+M)^2}\omega = \frac{mM}{m+M}a^2\omega \Rightarrow L = \mu a^2\omega$$

where $\mu = \frac{mM}{m+M}$ is called the reduced mass of the electron because it is less than m by a factor $\frac{1}{\left(1+\frac{m}{M}\right)}$

By taking nuclear motion into account, the energy of the electron in the n^{th} orbit of a one electron atom is

$$E_n' = -\frac{2\pi^2\mu Z^2 e^4}{(4\pi\varepsilon_0)^2 n^2 h^2}$$

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$$E'_n = E_n\frac{\mu}{m} = -\frac{13.6}{n^2}\frac{\mu}{m}\ (eV)$$

since, μ is slightly less than m, the electron energies are slightly less negative than if the nucleus were at rest (i.e. infinitely heavy). The wavelengths of spectral line computed on the basis of the above energy equation are slightly larger than those corresponding to an infinitely heavy nucleus and agree more closely with the experimental values.

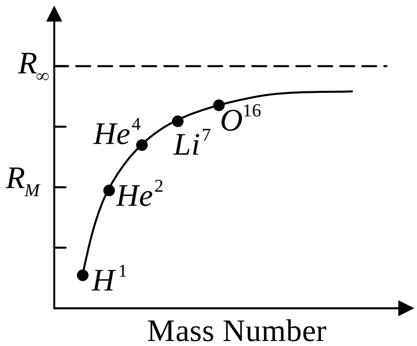
Orbital radius

$$r_n = 4\pi\in_0\frac{n^2\hbar^2}{\mu Ze^2} = a_0\frac{m}{\mu}$$

Variation of the Rydberg constant

The finite nuclear mass causes a slight variation in the Rydberg constant from atom to atom. The Rydberg constant for an infinitely heavy mass is

$$R_\infty = \frac{2\pi^2 me^4}{(4\pi\in_0)^2 ch^3}$$



and that for a nucleus of mass M is

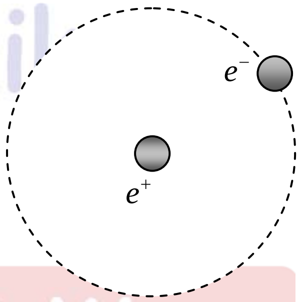
$$R_M = \frac{2\pi^2\mu e^4}{(4\pi\in_0)^2 ch^3} = \frac{2\pi^2 me^4}{(4\pi\in_0)^2 ch^3}\frac{\mu}{m} = R_\infty\frac{\mu}{m}$$

$$\Rightarrow R_M = \frac{R_\infty}{1+\frac{m}{M}}$$

Example: Positronium atom is bound state of positronium and electron.
(i) Find the energy expression for positronium atom.
(ii) Calculate energy, frequency, wavelength of L_α, L_β and H_α lines.

Solution: Reduce mass of positronium atom is

$$\mu = \frac{m_e^2}{m_e+m_e} = \frac{m_e}{2}$$



(i) Energy of the positronium atom is $E'_n = -\frac{13.6}{n^2}\times\frac{1}{2} = -\frac{6.8}{n^2}\ eV$ where n is the integer, representing the principle quantum state

For $n=1$; $E'_1 = -6.8\,eV$

For $n=2$; $E'_2 = -1.7\ eV$

For $n=3$; $E'_3 = -0.76\ eV$

(ii) Energy of the different series can be calculated as

For L_α line:

$$E_{L\alpha} = -1.7+6.8 = 5.1\ eV$$

$$\nu_{L\alpha} = 5.1\times 2.4\times10^{14} = 1.224\times10^{15}\ Hz$$

$$\lambda_{L\alpha} = \frac{c}{\nu_{L\alpha}} = 2.45\times10^{-7}\ m = 2450\ \overset{0}{\mathrm{A}}$$

For L_β line:

$$E_{L\beta} = -0.76+6.8 = 6.04\ eV$$

$$\nu_{L\beta} = 6.04 \times 2.4 \times 10^{14} = 1.449 \times 10^{15}\ Hz$$

$$\lambda_{L\beta} = 2.070 \times 10^{-7}\ m = 2070\ \overset{0}{\mathrm{A}}$$

For H_α line:

$$E_{H\alpha} = -0.76 + 1.7 = 0.94\ eV$$

$$\nu_{H\alpha} = 0.94 \times 2.4 \times 10^{14} = 2.256 \times 10^{14}\ Hz$$

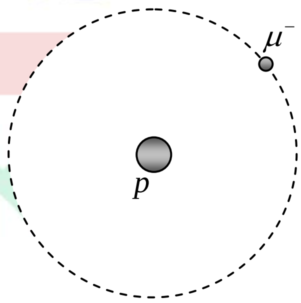
$$\lambda_{H\alpha} = \frac{c}{\nu_{L\alpha}} = 13.297 \times 10^{-7}\ m = 13297\ \overset{0}{\mathrm{A}}$$

Example: Muonic atom is bound state of proton and negative muon, where mass of muon and proton is $m_{\mu^-} = 207 m_e,\ m_p = 1836\, m_e$.

(a) Calculate the energy levels for muonic atom

(b) Calculate the energy of $L_\alpha,\ L_\beta$ and H_α

Solution: (a) The reduce mass of muonic atom is



$$\mu = \frac{m_{\mu^-} m_p}{m_\mu + m_p} = \frac{1836 \times 207}{1836 + 207} m_e$$

$$\frac{\mu}{m_e} = 186.03$$

$$E'_n = -\frac{13.6}{n^2} eV \times \frac{\mu}{m_e} = -\frac{13.6}{n^2} \times 186.03\, eV$$

For $n = 1$; $E'_1 = -2530\, eV$

For $n = 2$; $E'_2 = -632.5\, eV$

For $n = 3$; $E'_3 = -281.1\, eV$

(b) Energy of $L_\alpha,\ L_\beta$ and H_α lines is

$$E_{L\alpha} = E'_2 - E'_1 = -632.5 + 2530 = 1897.5 eV$$

$$E_{L\beta} = E'_3 - E'_1 = -281.1 + 2530 = 2248.9\, eV$$

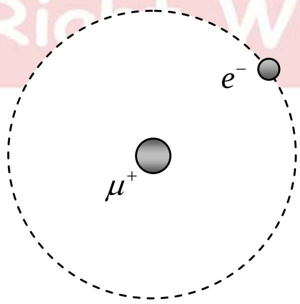
$$E_{H\alpha} = E'_3 - E'_2 = -281.1 + 632.5 = 351.4\, eV$$

Example: Muonium atom is formed when proton is replaced by positronium ($m_{\mu^+} = 207\, m_e$)

(i) Find energy expression

(ii) Calculate energy, frequency, wavelength of L_α, L_β and H_α lines.

Solution: (i) Reduced mass of muonium atom is



$$\mu = \frac{m_\mu m_e}{m_\mu + m_e} = \frac{207}{208} m_e = 0.995\, m_e$$

Energy of the atom is

$$E'_n = E_n\left(\frac{\mu}{m_e}\right) = -\frac{13.6}{n^2} \times 0.995 = -\frac{13.53}{n^2} eV$$

(ii) Energy of different lines is

$$E'_1 = -13.53\ eV\ ,\ E'_2 = -\frac{13.53}{4} = -3.38\, eV\ ,\ E'_3 = -\frac{13.53}{9} = -1.50\, eV$$

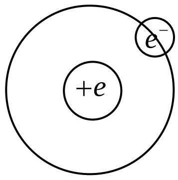
$$E_{L\alpha} = E'_2 - E'_1 = -3.38 + 13.53 = 10.15\ eV$$

$$\nu_{L\alpha} = \frac{E_{L\alpha}}{h} = \frac{10.15\times1.6\times10^{-19}}{6.6\times10^{-34}} = 2.436\times10^{15}$$

$$\lambda_{L\alpha} = \frac{c}{\nu_{L\alpha}} = \frac{3\times10^{8}}{2.436\times10^{15}} = 1.23\times10^{-7} = 1230\,\overset{0}{\text{A}}$$

Example: What is the velocity of electron in the ground state of Bohr's H - atom in terms of the speed of light? What is this called?

Solution: $u_n = \dfrac{e^2 z}{2\in_0 hn}$



$$\frac{u_1}{c} = \frac{e^2}{2\in_0 hn} = \frac{1}{137}$$

This is known as the fine structure constant.

Example: What will be the approximate quantum number n for an electron in an orbit of radius 0.1 mm?

Solution: $r_n = 0.53n^2 \quad (\overset{0}{\text{A}})$

$$10^6 = 0.53\,n^2$$

$$n^2 = \frac{10^6}{0.53} = 18.87\times10^5 \Rightarrow n = 1374$$

Example: The average life-time of an electron in an excited state of H - atom is about $10^{-8}s$. How many revolutions does an electron in the $n=2$ state make before its transition to $n=1$ state. The Rydberg constant for H - atom is $1.097\times10^7\ m^{-1}$.

Solution: $f = \dfrac{v_n}{2\pi r_n}$

$$v_n = \frac{Ze^2}{2\in_0 nh} \text{ and } r_n = \frac{n^2h^2\in_0}{\pi m Ze^2}$$

$$f = \frac{mZ^2e^4}{8\in_0^2 h^3}\left(\frac{2}{n^3}\right) = \frac{2R_H c}{n^3}$$

For $n=2$,

$$f = \frac{2\times1.097\times10^7\times3\times10^8}{8} = 8.2\times10^{14}s^{-1}$$

Number of revolutions

$$N = f\times10^{-8} = 8.2\times10^{14}\times10^{-8} = 8.2\times10^6$$

Example: If the mean wavelength of sodium D-lines is $5893\,\overset{0}{\text{A}}$, estimate the minimum energy in electron volt of the bombarding electron for excitation of these lines.

Solution: Wavelength of D - line $= 5893\times10^{-10}\,m$

Frequency of D - line $= \nu = \dfrac{c}{\lambda} = \dfrac{3\times10^8}{5893\times10^{-10}}Hz$

Energy of excitation of D - lines is

$$h\nu = \frac{6.62\times10^{-34}\times3\times10^8}{5893\times10^{-10}}J = 3.37\times10^{-19} = \frac{3.37\times10^{-19}}{1.6\times10^{-19}} = 2.1\,eV$$

Example: The first line of the Balmer series of hydrogen has a wavelength $6563\overset{0}{A}$. Calculate the wavelength of the second line.

Solution: $\frac{1}{\lambda_1} = R_H\left(\frac{1}{2^2}-\frac{1}{3^2}\right) = \frac{5R_H}{36}$, $\frac{1}{\lambda_2} = R_H\left(\frac{1}{2^2}-\frac{1}{4^2}\right) = \frac{3R_H}{16}$

$$\frac{\lambda_2}{\lambda_1} = \frac{5R_H}{36}\times\frac{16}{3R_H} = \frac{20}{27} \Rightarrow \lambda_2 = \lambda_1\times\frac{20}{27} = 6563\times\frac{20}{27} = 4861\overset{0}{A}$$

Example: Find the wavelength separation of the first member of the Balmer series due to ^1H and $^2H\left(={}^2D\right)$.

Solution: $\frac{1}{\lambda_H} = R_H\left(\frac{1}{2^2}-\frac{1}{3^2}\right) = \frac{5R_H}{36} \rightarrow \lambda_H = \frac{36}{5R_H}$

$$\frac{1}{\lambda_D} = \frac{36}{5R_H} \rightarrow \lambda_D = \frac{36}{5R_D}$$

$$R_H = \frac{R_\infty}{1+\frac{m}{M_H}},\ R_D = \frac{R_\infty}{1+\frac{m}{2M_H}} \Rightarrow \Delta\lambda = \frac{36}{5R_\infty}\left[1+\frac{m}{M_H}-1-\frac{m}{2M_H}\right] = \frac{36}{5R_\infty}\times\frac{m}{2M_H}$$

$$= \frac{36}{5\times1.097\times10^7}\times\frac{2}{1840} = 1.78\times10^{-10} = 1.78\overset{0}{A}$$

Example: Calculate the reduced mass, the Rydberg constant and the wavelength of the first Balmer line for positronium atom.

Solution: $\mu = \frac{m_e m_e}{m_e+m_e} = \frac{9.1\times10^{-31}}{2} = 4.55\times10^{-31}$ kg

$$R_{Positronium} = \frac{R_\infty}{1+\frac{m_{e^-}}{m_{e^+}}} = \frac{1.09\times10^7}{2} = 0.548\times10^7\ m^{-1}$$

$$\frac{1}{\lambda} = R_P\left(\frac{1}{2^2}-\frac{1}{3^2}\right) \Rightarrow \lambda = \frac{36}{5R_P} = \frac{36}{5\times0.548\times10^7} = 0.131\times10^{-5} = 13126\overset{0}{A}$$

or $\lambda = \frac{36}{5R_P} = \frac{36}{5R_H}\left(1+\frac{m_{e^-}}{m_{e^+}}\right)$

$$\lambda = \lambda_H\times2 = 2\times6563\overset{0}{A} = 13126\overset{0}{A}$$

Example: Find the wavelength of L_α, L_β lines of H - atom. Also, calculate wavelength of L_α, L_β of its two isotopes, deuterium and tritium.

Solution: For Hydrogen atom,

$$\mu = \frac{m_p m_e}{m_p+m_e} = \frac{1836m_e^2}{1837m_e} = 0.999456\ m_e \qquad E_n = -\frac{13.6}{n^2}eV$$

$$E_1 = -13.6\ eV,\ E_2 = -3.4\,eV,\ E_3 = -1.52\,eV$$

$$E_{L\alpha} = -3.4+13.6 = 10.2\,eV$$

$$E_{L\beta} = -1.52+13.6 = 12.08\ eV$$

$$\nu_{L\alpha} = 10.2 \times 2.4 \times 10^{14} = 2.448 \times 10^{15}\,Hz$$
$$\nu_{L\beta} = 12.08 \times 2.4 \times 10^{14} = 2.89 \times 10^{15}\,Hz$$
$$\lambda_{L\alpha} = \frac{c}{\nu_{L\alpha}} = 1.225 \times 10^{-7} = 1225\,\overset{0}{\text{A}}$$
$$\lambda_{L\beta} = \frac{c}{\nu_{L\beta}} = 1.038 \times 10^{-7} = 1038\,\overset{0}{\text{A}}$$

For Deuterium,

$$\mu = \frac{m_e m_d}{m_e + m_d} = \frac{3676\, m_e^2}{3677\, m_e} = 0.999728\, m_e$$
$$E_n' = E_n\left(\frac{\mu}{m_e}\right) = -\frac{13.6}{n^2} \times 0.999728 = -\frac{13.596}{n^2}\,eV$$
$$E_1 = -13.596\ eV,\ E_2 = -3.399\,eV,\ E_3 = -1.511eV$$
$$E_{L\alpha} = -3.399 + 13.596 = 10.197\,eV$$
$$\nu_{L\alpha} = 10.197 \times 2.4 \times 10^{14} = 2.4473 \times 10^{15}\,Hz$$
$$\lambda_{L\alpha} = \frac{c}{\nu_{L\alpha}} = 1.2258 \times 10^{-7} = 12258\,\overset{0}{\text{A}}$$

For Tritium,

$$\mu = \frac{m_e m_t}{m_e + m_t} = 0.999819\ m_e$$
$$E_n' = E_n\left(\frac{\mu}{m_e}\right) = -\frac{13.6}{n^2} \times 0.999819 = -\frac{13.5975}{n^2}\,eV$$
$$E_1 = -13.5975\,eV,\ E_2 = -3.3994\,eV,\ E_3 = -1.511eV$$
$$E_{L\alpha} = -3.399 + 13.596 = 10.197\,eV$$
$$\nu_{L\alpha} = 10.198 \times 2.4 \times 10^{14} = 2.4475 \times 10^{15}\,Hz$$
$$\lambda_{L\alpha} = \frac{c}{\nu_{L\alpha}} = 1.2257 \times 10^{-7} = 12257\,\overset{0}{\text{A}}$$

Example: The emission spectrum of the hydrogen atom is taken with a diffraction grating (line spacing $d = 2\,\mu m$). A line of the Balmer series is observed in the second order at an angle $\theta = 29^0 5'$. What is the quantum number of the excited state from which the transition starts?

Solution: $d\sin\theta = m\lambda$

$$\lambda = \frac{2 \times 10^{-6} \times \sin\left(29^0 5'\right)}{2} = 486.08\ nm$$

$$\frac{1}{\lambda} = R_\infty\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \Rightarrow \frac{1}{n^2} = \frac{1}{2^2} - \frac{1}{\lambda R_\infty} = \frac{1}{2^2} - \frac{1}{\lambda}\frac{36}{5R_\infty} \times \frac{5}{36} = \frac{1}{2^2} - \frac{6563}{4860} \times \frac{5}{36} = \frac{43740 - 32815}{174960}$$

$$\frac{1}{n^2} = \frac{1}{16} \Rightarrow n = 4$$

Example: The photons from the Balmer series in Hydrogen spectrum, having wavelengths between $450\,nm$ to $700\,nm$, are incident on a metal surface of work function $2\,eV$. Find the maximum kinetic energy of elected electron. (Given $hc = 1242\,eV\text{-}nm$)

Solution: For Balmer series,

$$\frac{hc}{\lambda} = 13.6\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$$

For $n = 3$, $\frac{1242\,eV\text{-}nm}{\lambda_3} = 13.6 \times \frac{5}{9 \times 4} \Rightarrow \lambda_3 = 657\,nm$

For $n = 4$, $\frac{1242\;eV\text{-}nm}{\lambda_4} = 13.6 \times \frac{3}{16} \Rightarrow \lambda_4 = 487\;nm$

$$K_{max} = \frac{hc}{\lambda} - w = \frac{1242}{487} - 2 = 2.55 - 2 = 0.55\,eV$$

Example: In hydrogen like atom $(Z = 11)$, n^{th} line of Lyman series has wavelength λ. The de-Broglie's wavelength of electron in the level from which it originated is also λ. Find the value of n.

Solution: $\frac{1}{\lambda} = R(11)^2\left(\frac{1}{1^2} - \frac{1}{n^2}\right)$ (i)

$$mvr_n = n\frac{h}{2\pi}, \quad \lambda = \frac{h}{mv}$$

$$\frac{r_n}{\lambda} = \frac{n}{2\pi} \qquad \text{(ii)}$$

From (i) and (ii)

$$\frac{n}{2\pi r_n} = R(11)^2\left(1 - \frac{1}{n^2}\right)$$

$$\frac{nZ}{2\pi a_0 n^2} = R(11)^z\left(1 - \frac{1}{n^2}\right)$$

$$n - \frac{1}{n} = \frac{1}{22\pi a_0 R} = \frac{1}{22 \times 3.14 \times 0.53 \times 10^{-10} \times 1.09 \times 10^7}$$

$$n - \frac{1}{n} = 25 \Rightarrow n^2 - 1 = 25n$$

$$n^2 \simeq 25n \qquad \text{as } n^2 >> 1$$

$$n \simeq 25$$

Example: An electron, in a hydrogen-like atom, is in an excited state. It has a total energy of $-3.4\,eV$. Calculate (i) the kinetic energy and (ii) the de-Broglie wavelength of the electron.

Solution:

(ii) de Broglie wavelength of electron

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mK}} = \frac{6.6 \times 10^{-34}}{\sqrt{2 \times (9.1 \times 10^{-31}) \times 3.4 \times 1.6 \times 10^{-19}}} \quad \lambda = 6.63 \times 10^{-10}\,m = 6.63\,\overset{0}{\text{A}}$$

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Example: A single electron orbits around a stationary nucleus of charge $+Ze$, where Z is a constant and e is the magnitude of the electronic charge. It requires $47.2eV$ to excite the electron from the second Bohr orbit to the third Bohr orbit. Find

(i) the value of Z

(ii) the energy required to excite the electron from the third to the fourth Bohr orbit

(iii) the wavelength of the electromagnetic radiation required to remove the electron from the first Bohr orbit to infinity.

(iv) the kinetic energy, potential energy and the angular momentum of the electron in the first Bohr orbit.

(v) the radius of the first Bohr orbit

Solution: (i) $E_3 - E_2 = -13.6Z^2\left(\frac{1}{3^2} - \frac{1}{2^2}\right)$

$$Z^2 = \frac{47.2\times 36}{13.6\times 5} = 25 \Rightarrow z = 5$$

(ii) $E_4 - E_3 = -13.6(5)^2\left(\frac{1}{4^2} - \frac{1}{3^2}\right) = 16.53eV$

(iii) $E_2 = E_1 = 13.6\times\frac{25}{1^2} = 340.0\ eV$

$$\lambda = \frac{12340}{340} = 36.4\overset{0}{\text{A}}$$

(iv) T.E. $= -340eV$

K.E. = |T.E.| $= 340eV$

P.E. $= 2\times$T.E.$= -680eV$

Angular momentum $= n\frac{h}{2\pi} = 1\times\frac{6.6\times 10^{-34}}{2\times 3.14} = 1.05\times 10^{-34}\ J\text{-}s$

(v) $r_1 = \frac{0.53}{Z}\overset{0}{\text{A}} = 0.106\overset{0}{\text{A}}$

Example: A μ- meson which is 210 times as heavy as an electron is captured by a proton to form a hydrogen-like atom.

(i) What is the energy of the photon that is emitted when μ- meson falls from the first excited state to the ground?

(ii) What is the radius of first Bohr orbit?

(iii) What is the velocity of μ- meson in the n^{th} circular Bohr orbit

Solution: Reduced mass $\mu = \frac{m_\mu m_P}{m_\mu m_P} = \frac{210\times 1836}{210+1836}m_e = 188.45m_e$

(i) $E_n' = -\frac{13.6}{n^2}\times\frac{\mu}{m_e}eV \Rightarrow h\nu_{2\to 1} = 13.6\left(\frac{1}{1^2} - \frac{1}{2^2}\right)\times 188.45 = 1922eV$

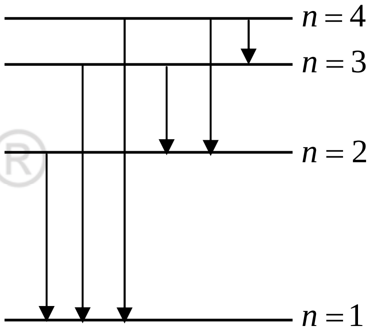
(ii) $r_1 = \frac{0.52}{\mu}\overset{0}{\text{A}} = \frac{0.52}{188.45} = 0.0028\overset{0}{\text{A}}$

(iii) The velocity v_n is independent of mass

$$v_n = \frac{2\pi Ze^2}{(4\pi\in_0)nh} = \alpha c = \frac{c}{137}$$

Example: Hydrogen atom, in its ground state, is excited by means of monochromatic radiation of wavelength $975\overset{0}{\text{A}}$. How many different lines are possible in the resulting spectrum? Calculate the longest wavelength amongst them. You may assume the ionization energy for hydrogen atom as $13.6 eV$.

Solution: $E(eV) = \dfrac{12375}{\lambda\left(\overset{0}{\text{A}}\right)} = \dfrac{12375}{975} = 12.69 eV$



$$E(eV) = 13.6\left(1 - \frac{1}{n^2}\right) \Rightarrow 12.69 = 13.6 - \frac{13.6}{n^2}$$

$$n^2 = \frac{13.6}{0.91} = 15 \Rightarrow n \simeq 4$$

Total number of lines $= \dfrac{n(n-1)}{2} = 6$

Longest wavelength is corresponding to $n = 4 \rightarrow n = 3$

$$E_4 - E_3 = 13.6\left(\frac{1}{9} - \frac{1}{16}\right) = 0.66\ eV \Rightarrow \lambda_{\max} = \frac{12375}{0.66} = 18750\overset{0}{\text{A}} = 1.875 \times 10^{-6}\ m$$

Example: A double ionized lithium atom is hydrogen-like atomic number 3.

(i) Find the wavelength of the radiation required to excite the electron in Li from the first to the third Bohr orbit. (ionization energy of the hydrogen atom equals $13.6 eV$)

(ii) How many spectral lines are observed in the emission spectrum of the above excited system?

Solution: (i) Excitation energy is

$$E_3 - E_1 = 13.6(3)^2\left[\frac{1}{1} - \frac{1}{9}\right] = 13.6 \times 9 \times \frac{8}{9} = 108.8\ eV$$

Excitation wavelength is

$$\lambda = \frac{12375}{108.8} = 113.7\overset{0}{\text{A}}$$

(ii) Total number of spectral lines $= \dfrac{n(n-1)}{2} = 3$