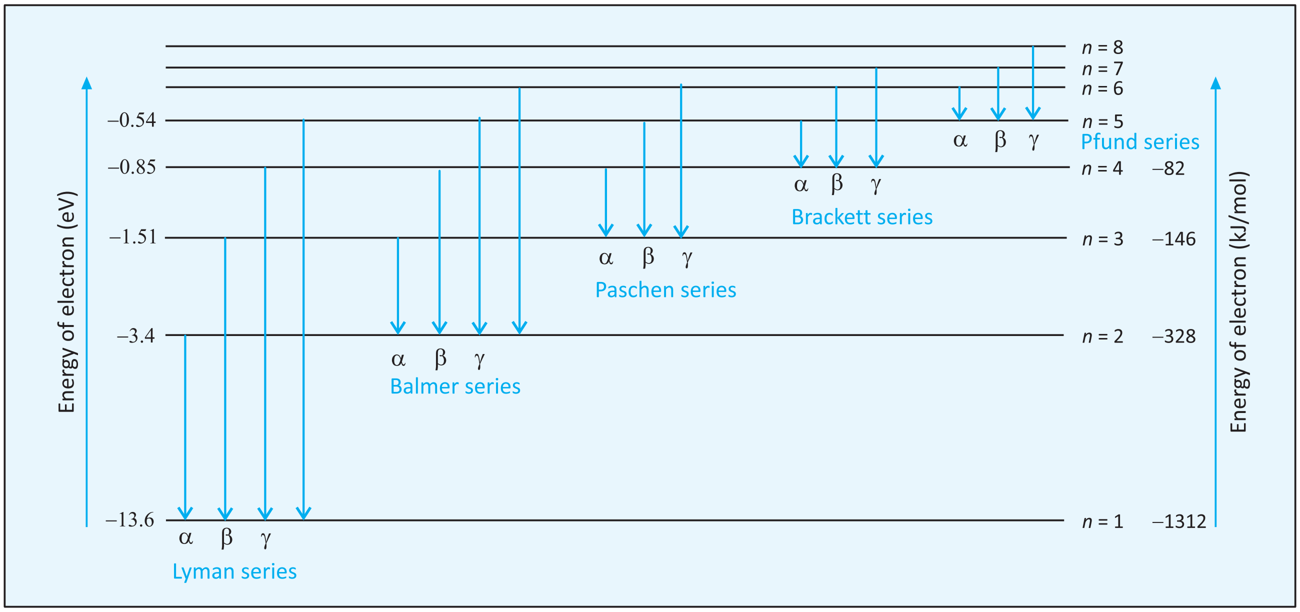
ENERGY LEVELS OF HYDROGEN ATOM SECTION - 4

The spectrum of H-atom studied by *Lyman*, *Balmer*, *Paschen*, *Brackett* and *Pfund* can now be explained on the basis of Bohr's Model.

It is now clear that when an electron jumps from a higher energy state to a lower energy state, the radiation is emitted in form of photons. The radiation emitted in such a transition corresponds to the spectral line in the atomic spectra of H-atom.



Spectral Lines and Energy Levels of Hydrogen atom

Lyman Series

When an electron jumps from any of the higher states to the ground state or Ist state ($n = 1$), the series of spectral lines emitted lies in *ultra-violet region* and are called as *Lyman Series*. The wavelength (or wave number) of any line of the series can be given by using the relation : $\bar{\nu} = R Z^2 \left(\frac{1}{1^2} - \frac{1}{n_2^2} \right)$ $n_2 = 2, 3, 4, 5, \ldots$

Note : For H-atom, $Z = 1$; He^+ ion, $Z = 2$ and Li^{2+}, $Z = 3$

Balmer Series

When an electron jumps from any of the higher states to the state with $n = 2$ (IInd state), the series of spectral lines emitted lies in *visible region* and are called as *Balmer Series*. The wave number of any spectral line can be given by using the relation : $\bar{\nu} = R Z^2 \left(\frac{1}{2^2} - \frac{1}{n_2^2} \right)$ $n_2 = 3, 4, 5, \ldots$

Paschen Series

When an electron jumps from any of the higher states to the state with $n = 3$ (IIIrd state), the series of spectral lines emitted lies in *near infra-red region* and are called as *Paschen Series*. The wave number of any spectral line can be given by using the relation : $\bar{\nu} = R Z^2 \left(\frac{1}{3^2} - \frac{1}{n_2^2} \right)$ $n_2 = 4, 5, 6, \ldots$

Brackett Series

When an electron jumps from any of the higher states to the state with $n = 4$ (IVth state), the series of spectral lines emitted lies in *far infra-red region* and called as *Brackett Series*. The wave number of any spectral line can be given by using the relation : $\bar{\nu} = RZ^2\left(\frac{1}{4^2} - \frac{1}{n_2^2}\right)$ $\quad n_2 = 5, 6, 7 \ldots.$

Pfund Series

When an electron jumps from any of the higher states to the state with $n = 5$ (Vth state), the series of spectral lines emitted lies in *far infra-red region* and are called as *Pfund Series*. The wave number of any spectral line can be given by using the relation : $\bar{\nu} = RZ^2\left(\frac{1}{5^2} - \frac{1}{n_2^2}\right)$ $\quad n_2 = 6, 7 \ldots.$

Note that Lyman series in UV region, Balmer series in visible region and Paschen, Brackett & Pfund series in Infra-red region are only for H-atom (Z = 1).

Note : In a particular series, First $[(n_1 + 1) \to n_1]$, second $[(n_1 + 2) \to n_1]$, third $[(n_1 + 3) \to n_1]$ . . . . lines are called as $\alpha, \beta, \gamma, \ldots$ .lines respectively. For example β–line in Balmer series corresponds to $(2 + 2) \to 2$ i.e., $4 \to 2$. In Lyman series : α – line $\equiv 2 \to 1$; β – line $\equiv 3 \to 1$; γ – line $\equiv 4 \to 1$.

The energy required to remove the electron from the outermost orbit of the atom in gaseous phase is called as *Ionisation energy*. Here, since we are considering only one electron species, Ionisation energy (IE) = $-E_1$ = $+13.6\,Z^2$ eV.

Illustration - 7 *The Lyman series of Hydrogen spectrum can be represented by the equation :*

$$\nu = 3.28 \times 10^{15}\left[\frac{1}{1^2} - \frac{1}{n^2}\right] s^{-1}$$ *. Calculate the maximum and minimum frequency in this series.*

SOLUTION :

Lyman frequency will be maximum corresponding to maximum energy transition. i.e. $1 \to \infty$

$$\Rightarrow \quad \nu_{max} = 3.28 \times 10^{15}\left[\frac{1}{1^2} - \frac{1}{\infty^2}\right] s^{-1} = 3.28 \times 10^{15}\ s^{-1}$$

Note that corresponding wavelength will be shortest wavelength.

And Lyman frequency will be minimum corresponding to minimum energy transition. i.e. $1 \to 2$

$$\Rightarrow \quad \nu_{min} = 3.28 \times 10^{15}\left[\frac{1}{1^2} - \frac{1}{2^2}\right] s^{-1} = 2.46 \times 10^{15}\ s^{-1}$$

Note that corresponding wavelength will be longest wavelength.

Illustration - 8 *The wavelength of second line (also called as β–line) in Balmer series of hydrogen atom is :*

(A) 656.28 Å **(B)** 4872 Å **(C)** 6562.8 Å **(D)** 486.2 Å

SOLUTION :

The transition responsible for second Balmer (β–line) line is $4 \to 2$. In H-atom, $n_1 = 2$ for Balmer series.

$$\Rightarrow \quad \Delta E = 13.6\,(1)^2\left(\frac{1}{2^2} - \frac{1}{4^2}\right) = 2.55 \text{ eV}$$

Now $\lambda = \frac{hc}{\Delta E} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{2.55 \times 1.6 \times 10^{-19}}$

$$\Rightarrow \quad \lambda = 4.872 \times 10^{-7}\ \text{m} = 4872\ \text{Å}$$

Hence correct option is (B).

Illustration - 9 *A spectral line in the spectrum of H-atom has a wave number of* 15222.22 cm^{-1}. *The transition responsible for this radiation is :* (*Rydberg constant R* = 109677 cm^{-1}).

(A) $2 \to 1$ **(B)** $4 \to 2$ **(C)** $3 \to 2$ **(D)** $2 \to 3$

SOLUTION :

$\lambda = 1/\bar{\nu} = 1/15222.22 = 6.569 \times 10^{-5}$ cm $= 6569$ Å

Clearly, it lies in Visible region i.e, in Balmer series.

Hence $n_1 = 2$

Using the relation for wave umber for H-atom:

$$\bar{\nu} = 1/\lambda = RZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$15222.22 = 109677\left(\frac{1}{2^2} - \frac{1}{n_2^2}\right)$$

$\Rightarrow$ $n_2 = 3$

$\Rightarrow$ the required transition is $3 \to 2$

Hence (C) is correct.

Note : (D) is wrong, since $2 \to 3$ will absorb radiation.

Drawbacks of Bohr model :

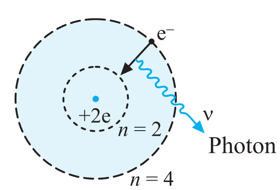
Bohr's model was successful in explaining the spectra and hence the structure of Hydrogen atom; still many questions were not answered.

- His postulates combined two different concepts : one from classical physics and second from modern theory of quantization.
- It could not explain the spectrum of atoms or ions having two or more electrons. It accounted only for the spectra of H-atom, He^+ ion and Li^{++} ion.
- There was no justification for the quantization of angular momentum of an electron, though this was a correct assumption.
- His model could not provide a satisfactory picture of Chemical Bond.
- It also failed to account for the brightness of the spectral lines, splitting spectral lines in electric field (Stark Effect) and in magnetic field (Zeeman Effect).

Illustration - 10 *Calculate the wavelength of light radiation that would be emitted, when an electron in the fourth Bohr's orbit of He*$^+$ *ion falls to the second Bohr's orbit. To what transition does this light radiation correspond in the H-atom ?*

SOLUTION :

First calculate the energy difference (ΔE) between 4th and 2nd Bohr orbit using :



$$\Delta E_{(4\to2)} = 13.6\ Z^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)\text{eV}$$

Substituting $n_1 = 2$ and $n_2 = 4$, $Z = 2$ we get ;

$$\Delta E = 10.2\ \text{eV}$$

This energy difference (energy lost by the electron) will be equal to the energy of the emitted photon.

Using : $\lambda = \dfrac{12400}{E_{Photon}(\text{eV})}$ Å $= \dfrac{12400}{10.2}$ Å $= 1215.7$ Å

Note : The emitted radiation is in UV region which implies that, in H-atom this transition would lie in Lyman Series ($n_1 = 1$).

Hence our aim is now to find the transition : $n_2 \rightarrow 1$

Use : $\Delta E_{(n_2 \rightarrow 1)} = 13.6 \times 1^2 \left(\frac{1}{1^2} - \frac{1}{n_2^2}\right) eV \quad \Rightarrow \quad 10.2 = 13.6\left(1 - \frac{1}{n_2^2}\right) eV \quad \Rightarrow \quad n_2 = 2$

Hence the corresponding transition in H-atom is $2 \rightarrow 1$

Note : This concept can be applied only for H-atom.

Alternate Approach :

As discussed above : $\Delta E_{(4 \rightarrow 2)} \text{ (in } He^+) = \frac{hc}{\lambda_{Photon}} = 13.6 \times 2^2 \times \left(\frac{1}{2^2} - \frac{1}{4^2}\right) eV$ ....(i)

$\Delta E_{(n_2 \rightarrow n_1)} \text{ (in H)} = \frac{hc}{\lambda_{Photon}} = 13.6 \times 1^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) eV$ ....(ii)

Try to convert equation (ii) in the form given in equation (i) and compare it with equation (i) as below :

$\Rightarrow \quad \Delta E_{(4 \rightarrow 2)} \text{ (in } He^+) = \frac{hc}{\lambda_{Photon}} = 13.6 \times 1^2 \times \left(\frac{1}{1^2} - \frac{1}{2^2}\right) eV$ [2^2 shifted inside]

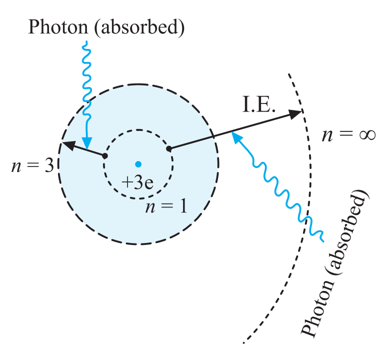
On comparing the above equation with equation (i), we get : $n_1 = 1$ and $n_2 = 2$

Note : This concept can be applied for any H-like species.

Illustration - 11 *Find the wavelength of radiation required to excite the electron in ground level of Li^{++} (Z = 3) to third energy level. Also find the ionisation energy of Li^{2+}. (R = 109, 677 cm^{-1})*

SOLUTION :

Ground level : n = 1



Use : $\frac{1}{\lambda} = RZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

Putting the values : $n_1 = 1, n_2 = 3, Z = 3$

We get : $\frac{1}{\lambda} = 109677 \times 3^2 \times \left(\frac{1}{1^2} - \frac{1}{3^2}\right)$

$\Rightarrow \quad \frac{1}{\lambda} = 877416 \, cm^{-1} \quad \Rightarrow \quad \lambda = \frac{1}{\bar{v}} = 113.97 \text{ Å}$

Ionisation energy is the energy required to remove the electron from ground state to infinity i.e. corresponding transition responsible is $1 \rightarrow \infty$.

i.e. $\quad \Delta E_{(1 \rightarrow \infty)} = 13.6 \times 3^2 \left(\frac{1}{1^2} - \frac{1}{\infty^2}\right) eV$

Ionisation energy = $\Delta E_{(1 \rightarrow \infty)} = 122.4 \text{ eV} = 1.95 \times 10^{-17} \text{ J} \quad \left[\because 1 eV = 1.6 \times 10^{-19} J\right]$

Note : Ionisation Energy (IE) = $-E_1 = +13.6 Z^2$ eV

Illustration - 12 *Find the energy released (in ergs) when 2.0 gm atom of Hydrogen atoms undergo transition giving spectral line of lowest energy in visible region of its atomic spectra.*

SOLUTION :

For H–atom, the spectral lines in visible region correspond to Balmer Lines ($n_1 = 2$). Now for lowest energy photon, the required transition will be from $3 \rightarrow 2$.

Using the relation for ΔE :

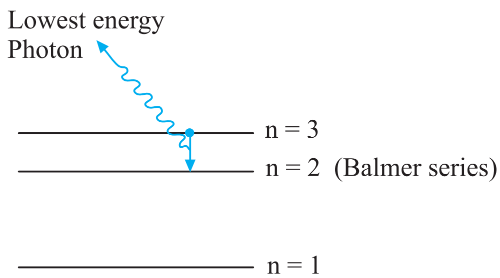
$$\Delta E = 2.18 \times 10^{-18}\,(1)^2 \left(\frac{1}{2^2} - \frac{1}{3^2}\right) \text{J / atom}$$

$$= 3.03 \times 10^{-19}\ \text{J}$$

Now for 2.0 *gm–atoms*, the energy released will be

$$E = (2 \times 6.023 \times 10^{23}) \times 3.03 \times 10^{-19}\ \text{J}$$

$$= 3.65 \times 10^{5}\ \text{J} \equiv 3.65 \times 10^{12}\ \ [1\text{J} \equiv 10^{7}\ \text{ergs}]$$



IN-CHAPTER EXERCISE - B

1. *Calculate the longest wavelength, which can remove the electron from 2nd Bohr orbit to infinity in Li^{2+} ion. Given E_1 for H-atom = 13.6 eV.*

2. *What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition n = 4 to n = 2 of He^{+} spectrum ?*

3. *The wavelength of a certain line in the H-atom spectra is observed to be 434.1 nm for hydrogen atom. To what value of n_2 does this line correspond ? Given : Rydberg constant = 109677 cm^{-1} .*

4. *When an electron makes a transition from n = 3 to n = 1 in a Hydrogen atom, find the change in potential energy of the atom.*

5. *Given ionisation potential of H atom is 13.6 eV. Find the frequency and wavelength of H_β line of Balmer series.*

6. *Calculate :*
- **(a)** *The series limit for Balmer series of H spectrum.*
- **(b)** *Ionisation energy of H atom.*
- **(c)** *Wavelength of the photon that would ionize this H atom.*

7. *The first IE of potassium is 100 kcal mole^{-1}. Calculate the lowest possible frequency of light that can ionise a potassium atom.*

Choose the correct alternative. Only One choice is Correct. However, questions marked with '*' may have More than One correct option :

***8.** *The wavelength of a spectral line for an electronic transition is inversely related to :*
- **(A)** *the number of orbit undergoing the transition*
- **(B)** *the square of nuclear charge of an atom*
- **(C)** *the difference in energy levels involved in the transition*
- **(D)** *the velocity of the electron undergoing the transition*

9. *In the hydrogen atom, the transition energy will be maximum for*

(A) $n_5 \rightarrow n_4$ **(B)** $n_4 \rightarrow n_3$ **(C)** $n_3 \rightarrow n_2$ **(D)** *will be the same in all transitions*

10. *If the radius of the first Bohr orbit of the H atom is r then for the Li^{2+} ion it will be*

(A) 3*r* **(B)** 9*r* **(C)** *r*/3 **(D)** *r*/9

11. *The wavelength of certain line in H-atom spectra is observed to be* 4341 Å. ($R_H = 109677\ cm^{-1}$). *The value of quantum number of higher state is :*

(A) 3 **(B)** 4 **(C)** 5 **(D)** *Data insufficient*

12. *A certain transition in H-spectrum from an excited state to ground state in one or more steps gives rise to a total of ten lines. How many of these belong to visible spectrum ?*

(A) 3 **(B)** 4 **(C)** 5 **(D)** 6

13. *According to Bohr model, angular momentum of an electron in the 3rd orbit is :*

(A) $\frac{3h}{\pi}$ **(B)** $\frac{1.5h}{\pi}$ **(C)** $\frac{3\pi}{h}$ **(D)** $\frac{9h}{\pi}$

14. *An electron in H-atom is moving with a kinetic energy of* 5.45×10^{-19} J. *What will be energy level for this electron ?*

(A) 1 **(B)** 2 **(C)** 3 **(D)** *None of these*

15. *An electron jumps from 6th energy level to 3rd energy level in H-atom, how many lines belong to visible region ?*

(A) 1 **(B)** 2 **(C)** 3 **(D)** *Zero*

***16.** *Which of the following is(are) proportional to the energy of electromagnetic radiation ?*

(A) *Frequency* **(B)** *Wave number* **(C)** *Wavelength* **(D)** *Number of photons*

17. *Which of the following best describes the emission spectrum of atomic hydrogen ?*

(A) *A discrete series of lines of equal intensity and equally spaced with respect to wavelength*

(B) *A series of only four lines*

(C) *A continuous emission of radiation of all frequencies*

(D) *Several discrete series of lines with both intensity and spacing between lines decreasing as the wave number increases with each series*

***18.** *According to Bohr's theory :*

(A) *when the atom gets the required energy from the outside, electrons jumps from lower orbits to higher orbits and remain there*

(B) *when the atom gets the required energy from outside, electrons jumps from lower orbits to higher orbits and remain there for very short intervals of time and return back to the lower orbit, radiating energy*

(C) *angular momentum of the electron is proportional to n*

(D) *angular momentum of the electron is independent of n*

19. *If uncertainty in position of electron is zero, the uncertainty in its momentum would be :*

(A) *zero* **(B)** $h/2\pi$ **(C)** $h/4\pi$ **(D)** *infinity*

20. *If* E_1, E_2 *and* E_3 *represent respectively the kinetic energies of an electron, an alpha particle and a proton each having same de Broglie wavelength then :*

(A) $E_1 > E_3 > E_2$ **(B)** $E_2 > E_3 > E_1$ **(C)** $E_1 < E_3 < E_2$ **(D)** $E_1 = E_2 = E_3$

***21.** *Which of the following parameters are not same for all hydrogen like atoms and ions in their ground state ?*

(A) *Radius of orbit* **(B)** *Speed of electron*

(C) *Energy of the atom* **(D)** *Orbital angular momentum of electron*

***22.** *Given ionisation potential of H atom is 13.6 eV. The frequency of* H_β *line of Lyman series is :*

(A) $2.90\times10^{15}\ Hz$ **(B)** $3.07\times10^{15}\ Hz$

(C) $1.02\times10^{7}\ Hz$ **(D)** $9.7\times10^{6}\ Hz$

23. *In which of the following system will the radius of the first orbit* ($n = 1$) *be minimum* ?

(A) *hydrogen atom*　**(B)** *deuterium atom*

(C) *singly ionized helium*　**(D)** *doubly ionized lithium*

24. *In which of the following system will the wavelength corresponding to* $n = 2$ *to* $n = 1$ *be minimum* ?

(A) *hydrogen atom*　**(B)** *deuterium atom*

(C) *singly ionized helium*　**(D)** *doubly ionized lithium*

25. *The energy of an atom (or ion) in its ground state is* 54.4 *eV*. *It may be* :

(A) *hydrogen*　**(B)** *deuterium*　**(C)** He^+　**(D)** Li^{++}

26. *A hydrogen atom in ground state absorbs* 10.2 *eV of energy*. *The orbital angular momentum of the electron is increased by*:

(A) 1.05×10^{-34} *J-s*　**(B)** 2.11×10^{-34} *J-s*　**(C)** 3.16×10^{-34} *J-s*　**(D)** 4.22×10^{-34} *J-s*

27. *A photon was absorbed by a hydrogen atom in its ground state and the electron was promoted to the fifth arbit. When the excited atom returned to its ground state, visible and other quanta were emitted. Other quanta are* :

(A) $2 \to 1$　**(B)** $5 \to 2$　**(C)** $3 \to 1$　**(D)** $4 \to 1$

28. *Of the following, radiation with maximum wavelength is* :

(A) *UV*　**(B)** *Radio wave*　**(C)** *X-ray*　**(D)** *IR*

29. *Zeeman effect explain splitting of lines in* :

(A) *Magnetic field*　**(B)** *Electron field*　**(C)** *Both*　**(D)** *None of these*

WAVE NATURE OF PARTICLES　　SECTION - 5

We have studied that light shows dual nature i.e. wave nature (*Electromagnetic Radiation*) and particle nature (*photons*). In the following article we will see that not only light but *matter also shows dual nature*.

In 1923, de Broglie suggested that, since light is dualistic in nature: behaving in some aspects as waves and in others like particles, the same might be true of matter. According to him, every form of matter (electron or proton or any other particle) behaves like waves in some circumstances. These were called as *matter waves* or *de Broglie waves*. de Broglie postulated that a particle of mass *m* moving with a velocity v should have a wavelength λ given by :

$$\lambda = \frac{h}{p} = \frac{h}{mv} \qquad (p = \text{linear momentum} = mv)$$

Now we can think of a model of atom where moving electrons (obviously around the nucleus) should behave like waves. The wave hypothesis of de Broglie was later developed by Heisenberg, Schrödinger, Fermi and many others in modern atomic theory and is known as *wave mechanics* or *quantum mechanics*.

In new theory, electrons in an atom are visualised as diffused clouds surrounding the nucleus. The idea that the electrons in an atom move in definite orbits (*Bohr's model*) is now abandoned. The new theory assigns definite energy states to an atom but discards a definite path for movement of an electron.