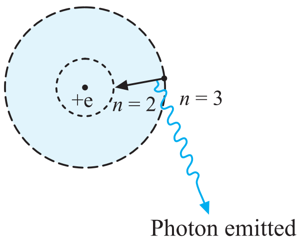
SUBJECTIVE SOLVED EXAMPLES

Example - 1 *Calculate the wavelength and wave number of the spectral line when an electron in H-atom falls from higher energy state n = 3 to a state n = 2. Also determine the energy of a photon to ionize this atom by removing the electron from 2nd Bohr's orbit. Compare it with the energy of photon required to ionize the atom by removing the electron from the ground state.*

SOLUTION :



First calculate the energy (ΔE) between the Bohr orbits n = 3 and n = 2 using :

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

$$\Delta E_{(3 \to 2)} = 13.6\ (1)^2 \left(\frac{1}{2^2} - \frac{1}{3^2}\right) \text{eV}$$

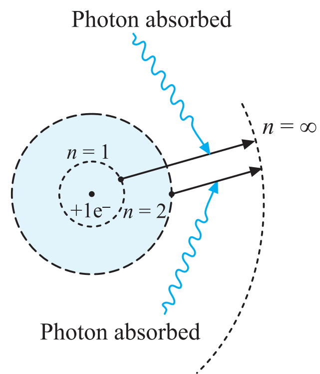
$$= 1.89 \text{ eV}$$

Now this energy difference is the energy of the photon emitted.

$$\Rightarrow \quad E_{\text{Photon}} = \frac{12400}{\lambda \text{ (in Å)}} \text{eV}$$

$$\Rightarrow \quad \lambda = \frac{12400}{1.89} = 6560.3 \text{ Å}$$

$$\text{and} \quad \bar{\nu} = \frac{1}{\lambda} = 1.52 \times 10^6 \text{m}^{-1}$$



- To ionize the atom from $n = 2$, the transition will be $n = 2 \to n = \infty$.

$$\Delta E_{(2 \to \infty)} = 13.6 \times 1^2 \times \left(\frac{1}{2^2} - \frac{1}{\infty^2}\right) \text{eV}$$

$$= 3.4 \text{ eV}$$

- To ionize the atom from ground state (n = 1), the transition is $1 \to \infty$.

$$\Delta E = 13.6 \text{ eV} \times 1^2 \times \left(\frac{1}{1^2} - \frac{1}{\infty^2}\right) = 13.6 \text{ eV}$$

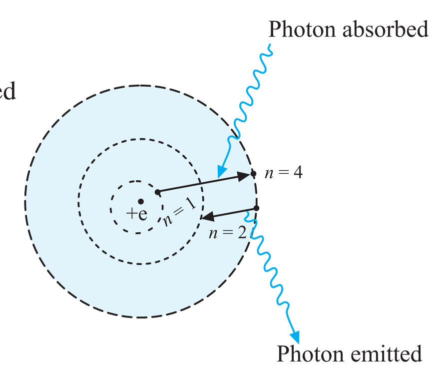
Example - 2 *A hydrogen atom in the ground state is hit by a photon exciting the electron to 3rd excited state. The electron then drops to 2nd Bohr orbit. What is the frequency of radiation emitted and absorbed in the process ?*

SOLUTION :

Energy is absorbed when electron moves from ground state ($n = 1$) to 3rd excited state ($n = 4$).

First calculate the energy difference between n = 1 and n = 4.

$$\text{Use :} \quad \Delta E_{(1 \to 4)} = 2.18 \times 10^{-18} \times Z^2 \times \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right);$$



Here $Z = 1, n_1 = 1, n_2 = 4$

$$\Rightarrow \Delta E_{(1 \to 4)} = 2.18 \times 10^{-18} \times 1^2 \times \left(\frac{1}{1^2} - \frac{1}{4^2}\right) J$$

$$= 2.04 \times 10^{-18} \text{ J}$$

This is the energy of the photon absorbed.

Use : $E_{Photon} = h\nu = 2.04 \times 10^{-18} J$ to get :

$$\Rightarrow \nu = 3.08 \times 10^{15} \text{ Hz}$$

- Similarly, when electron jumps from n = 4 to n = 2, energy is emitted and is given by the same relation.

Put $n_1 = 2$ and $n_2 = 4$ in the expression of ΔE, to get :

$$\Delta E_{(4 \to 2)} = 2.18 \times 10^{-18} \times 1^2 \times \left(\frac{1}{2^2} - \frac{1}{4^2}\right) J$$

$$= 4.08 \times 10^{-19} \text{ J}$$

This is the energy of the photon emitted.

Use : $E_{Photon} = h\nu = 4.08 \times 10^{-19}$ J

$$\Rightarrow \nu = 6.16 \times 10^{14} \text{ Hz}$$

Example - 3 *A hydrogen like ion, He⁺ (Z = 2) is exposed to electromagnetic waves of 256.2 Å. The excited electron gives out induced radiations. Find the wavelength of the induced radiations, when electron de-excites back to the ground state.* $R = 109737 \text{ cm}^{-1}$.

SOLUTION :

He^+ ion contains only one electron, so Bohr's model is applicable here. It absorbs a photon of wavelength $\lambda = 256.4$ Å. Assume the electron to be in ground state initially. Let it jumps to an excited state n_2.

Use the relation, to find n_2.

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

Substitute for $\lambda = 256.2 \text{ Å} = 256.2 \times 10^{-8}$ cm,

$R = 109737, Z = 2$ for He^+ ion, $n_1 = 1$

Now, Find n_2.

$$\frac{1}{256.2 \times 10^{-8}} = 109737 \times (2)^2 \left(\frac{1}{1_1^2} - \frac{1}{n_2^2}\right)$$

$$\Rightarrow n_2 = 3$$

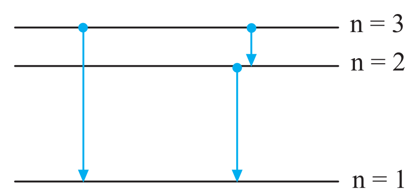
From $n = 3$, the electron can fall back to the ground state in three possible ways (transitions) :

$$3 \to 1, \quad 3 \to 2, \quad 2 \to 1$$

Hence three possible radiations are emitted. Find the wavelengths corresponding to these transitions.

The wavelength (λ) for transition, $3 \to 1$ will be same i.e., 256.4Å. Find λ for $3 \to 2$ and $2 \to 1$ using the same relation.

$$\lambda(3 \to 1) = 256.4 \text{ Å}, \lambda(3 \to 2) = 1641.3 \text{ Å},$$
$$\lambda(2 \to 1) = 303.9 \text{ Å}$$



Example - 4 *Hydrogen gas when subjected to photo-dissociation, yields one normal atom and one atom possessing 1.97 eV more energy than normal atom. The bond dissociation energy of hydrogen molecule into normal atoms is 103 kcal mol⁻¹. Compute the wave length of effective photon for photo dissociation of hydrogen molecule in the given case.*

SOLUTION :

$$H_2 \rightarrow H + H^*$$

where H is normal H-atom and H^* is excited H-atom.

So the energy required to dissociate H_2 in this manner will be greater than the usual bond energy of H_2 molecule.

$$E(absorbed) = \textit{dissociation energy of } H_2 + \textit{extra energy of excited atom}$$

Energy required to dissociate in normal manner

$= 103 \times 10^3$ cal per mol *(given)*

$$= \frac{103 \times 10^3 \times 4.18}{6 \times 10^{23}} = 7.17 \times 10^{-19} \text{ J/molecule}$$

The extra energy possessed by excited atom is 1.97 eV

$$\equiv 1.97 \times 1.6 \times 10^{-19}\text{ J} = 3.15 \times 10^{-19}\text{ J}$$

$$E\,(\text{absorbed}) = 7.175 \times 10^{-19} + 3.15 \times 10^{-19}\text{ J}$$

$$= 1.03 \times 10^{-18}\text{ J}$$

Now calculate the wavelength of photon corresponding to this energy.

$$E_{photon} = \frac{hc}{\lambda} = 1.03 \times 10^{-18}\text{ J}$$

$$\Rightarrow \quad \lambda = 1930\text{ Å}$$

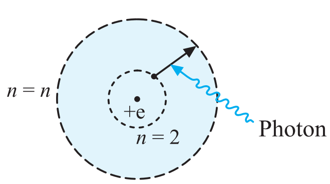
Example - 5 *An electron in the first excited state of H-atom absorbs a photon and is further excited. The de Broglie wavelength of the electron in this state is found to 13.4 Å. Find the wavelength of photon absorbed by the electron in Å. Also find the longest and shortest wavelength emitted when this electron de-excites back to ground state.*

SOLUTION :

Note : The energy state n = 1 is known as Ground State
The energy state n = 2 is known as First Excited State.
The energy state n = 3 is known as Second excited State and so on.

The electron from $n = 2$ absorbs a photon and is further excited to a higher energy level (*let us say n*).

The electron in this energy level (n) has a de Broglie wavelength $(\lambda) = 13.4$ Å.



$$\lambda_e = \frac{h}{m_e v_e}$$

and $\quad v_e = 2.18 \times 10^6 \dfrac{Z}{n}\text{ ms}^{-1}$

[v_e is the velocity of e^- in nth Bohr orbit]

$$\Rightarrow \quad v_e = \frac{h}{\lambda m} = 2.18 \times 10^6 \left(\frac{1}{n}\right)$$

$$\Rightarrow \quad \frac{6.626 \times 10^{-34}}{\left(13.4 \times 10^{-10}\right) \times \left(9.1 \times 10^{-31}\right)} = 2.18 \times 10^6 \times \frac{1}{n}$$

$$\Rightarrow \quad n = 4$$

Now find the wavelength of the photon responsible for the excitation from n = 2 to $n = 4$

Using the relation :

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

$$= 2.55\text{ eV} \qquad [n_1 = 2, n_2 = 4, Z = 1]$$

$$\Rightarrow \quad \Delta E_{(2 \to 4)} = \frac{12400}{\lambda\,(\text{in Å})}\text{ eV}$$

$$\Rightarrow \quad \lambda = \frac{12400}{2.55}\text{Å} = 4863.1\text{ Å}$$

The longest wavelength emitted when this electron (*from n* = 4) falls back to the ground state will corresponds to the minimum energy transition.

The transition corresponding to minimum energy will be $4 \to 3$.

Note : *The transition corresponding to maximum energy will be* $4 \to 1$.

$$\Delta E_{(\text{Energy diff.})} = E_{\text{Photon}} = \frac{hc}{\lambda} = h\nu$$

$$\Rightarrow \quad \Delta E \propto \frac{1}{\lambda_{\text{Photon}}} \quad \text{or} \quad \Delta E \propto \nu_{\text{Photon}}$$

Using the same relation :

$$\Delta E_{(4 \to 3)} = 13.6\ Z^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) eV$$

$$[n_1 = 3, n_2 = 4, Z = 1]$$

$$\Rightarrow \quad \Delta E_{(4 \to 3)} = 0.66 \text{ eV}$$

$$\Delta E = E_{\text{Photon}} = \frac{12400}{\lambda \text{ (in Å)}} \text{ eV}$$

$$\Rightarrow \quad \lambda = 18752.8 \text{ Å}$$

Shortest wavelength : $4 \to 1$

$$\Delta E_{(4 \to 1)} = 13.6 \times 1^2 \times \left(\frac{1}{1^2} - \frac{1}{4^2}\right) eV$$

$$= 12.75 \text{ eV}$$

$$\Rightarrow \quad \Delta E_{(4 \to 1)} = E_{\text{Photon}} = \frac{12400}{\lambda \text{ (in Å)}} \text{ eV}$$

$$\Rightarrow \quad \lambda = 973.2 \text{Å}$$

Example - 6 *A single electron orbits around a stationary nucleus of charge +Ze, where Z is a constant and e is the magnitude of electronic charge. It requires 47.2 eV to excite the electron from second Bohr orbit to the third Bohr. Find :*

(a) *the value of Z*

(b) *the energy required to excite the electron from n = 3 to n = 4*

(c) *the wavelength of radiation required to remove electron from 2nd Bohr's orbit to infinity*

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

(e) *the ionisation energy of above one electron system in eV.*

SOLUTION :

Since the nucleus has a charge +Ze, the atomic number of the ion is 'Z'.

(a) The transition is $n_1 = 2 \to n_2 = 3$ by absorbing a photon of energy 47.2 eV.

$$\Rightarrow \quad \Delta E = 47.2 \text{ eV}$$

Using the relation :

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

$$\Rightarrow \quad 47.2 = 13.6 Z^2\left(\frac{1}{2^2} - \frac{1}{3^2}\right) \quad \Rightarrow \quad Z = 5$$

(b) The required transition is $n_1 = 3 \to n_2 = 4$ by absorbing a photon of energy ΔE.

Find ΔE by using the relation :

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

$$\Rightarrow \quad \Delta E = 13.6 (5)^2\left(\frac{1}{3^2} - \frac{1}{4^2}\right) eV$$

$$\Rightarrow \quad \Delta E = 16.53 \text{ eV}$$

(c) The required transition is $n_1 = 2 \to n_2 = \infty$ by absorbing a photon of energy ΔE.

Find ΔE by using the relation :

$$\Delta E = 13.6\ (5)^2 \left(\frac{1}{2^2} - \frac{1}{\infty^2}\right) \Rightarrow \Delta E = 85\ \text{eV}$$

Find λ of radiation corresponding to energy 85 eV.

$$\Rightarrow \quad \lambda = \frac{12400}{85}\ \text{Å}$$

$$= 146.16\ \text{Å}$$

(d) If energy of electron be E_n, then $KE = -E_n$ and $PE = 2E_n$

$$E_n = \frac{-13.6\ Z^2}{n^2} = \frac{-13.6\times5^2}{1^2} = -340\ \text{eV}$$

$$KE = -(-340\ \text{ev}) = 340\ \text{eV}$$

$$PE = 2\,(-340\ \text{eV}) = -680\ \text{eV}$$

$$\text{Angular momentum } (\ell) = n\left(\frac{h}{2\pi}\right)$$

$$\Rightarrow \quad \ell = 1\times\left(\frac{6.626\times10^{-34}}{2\pi}\right)$$

$$= 1.05\times10^{-34}\ \text{J-s}$$

Note : Angular momentum of e^- is also equal to $m_e v_e r$.

(e) The ionisation energy (IE) is the energy required to remove the electron from ground state to infinity. So the required transition is $1 \to \infty$. The ionisation energy $(IE) = -E_1 = 13.6\,(Z)^2\ \text{eV}$

$\Rightarrow \quad 1E = +13.6\times5^2 = 340\ \text{eV}.$

Example - 7 *The hydrogen-like species Li^{2+} is in a spherically symmetric state S_1 with one radial node. Upon absorbing light the ion undergoes transition to a state S_2. The state S_2 has one radial node and its energy is equal to the ground state energy of the H-atom.*

(i) *The state S_1 is :*

(A) 1*s* **(B)** 2*s*

(C) 2*p* **(D)** 3*s*

(ii) *Energy of the state S_1 in units of the hydrogen atom ground state energy is :*

(A) 0.75 **(B)** 1.50

(C) 2.25 **(D)** 4.50

(iii) *The orbital angular momentum quantum number of the state S_2 is :*

(A) 0 **(B)** 1

(C) 2 **(D)** 3

SOLUTION : **(i)-(B) (ii)-(C) (iii)-(B)**

Radial node $= n - \ell - 1$

$S_1 \equiv 2s$ (As it is spherically symmetric and has one radial node)

$S_2 \equiv 3p$ (As its energy is equal to ground state energy of H-atom hence, its principal quantum number is 3 and it contains only 1 radial node)

Hence its Orbital angular momentum quantum number is 1. $(1 = 3 - \ell - 1 \Rightarrow \ell = 1)$

Energy of electron in S_1

$$= -13.6\times\frac{Z^2}{n^2}\text{eV} = -13.6\times\frac{3^2}{2^2}\ \text{eV}$$

Energy of hydrogen in ground state $= -13.6$ eV

$\Rightarrow$ Energy of electron in S_1 is 2.55 times the energy hydrogen atom in ground state.

Example - 8 *Find the energy required to excite 1.10 litre of hydrogen atoms gas at 1.0 atm and 298 K to the first excited state of atomic hydrogen. The energy required for the dissociation of H–H bond is 436 kJ/mol. Also calculate the minimum frequency of a photon to break this bond.*

SOLUTION :

Let us, first find the number of moles of hydrogen atoms.

$$n_{H_2} = \frac{PV}{RT} = \frac{1\times1.10}{0.0821\times298} = 0.045$$

Thus the energy required to break 0.045 moles of H_2 (H–H bond) = $0.045 \times 436 = 19.62$ kJ.

Now calculate the energy needed to excite the H–atoms to first excited state i.e., to $n = 2$ (First excited state is referred to $n = 2$).

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

$$= 1.635 \times 10^{18} \text{ J/atom}$$

No. of H atoms = (No. of H_2 molecules) × 2

$$= (0.05 \times 6.02 \times 10^{23}) \times 2 = 6.02 \times 10^{22}$$

The energy required to excite the given number of H–atoms $= 6.02 \times 10^{22} \times 1.635 \times 10^{-18}$ J = 98.43 kJ

So the total energy required

$$= 19.62 + 98.43 = 118.05 \text{ kJ}$$

Now the energy required to break a single

$$\text{H-H bond} = \frac{436 \times 10^3}{6.023 \times 10^{23}} = 7.238 \times 10^{-19} \text{ J/atm}$$

= Energy supplied by the photon

$$\Rightarrow \quad 7.238 \times 10^{-19} = h\nu = 6.626 \times 10^{-34} (\nu)$$

$$\Rightarrow \quad \nu = 1.09 \times 10^{15} \text{ Hz.}$$

Example - 9 *Estimate the difference in energy between 1st and 2nd Bohr's orbit for a H–atom. At what minimum atomic number (Z), a transition from n = 2 to n = 1 energy level would result in the emission of radiation with wavelength $\lambda = 3.0 \times 10^{-8}$ m ? Which Hydrogen atom like species this atomic number corresponds to ? How much ionisation potential is needed to ionise this species ? ($R = 1.097 \times 10^7\ m^{-1}$)*

SOLUTION :

The difference in energy is given by ΔE :

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

$$= 1.65 \times 10^{-18} \text{ J} \equiv 1.65 \times 10^{-11} \text{ ergs} \equiv 10.2 \text{ eV}$$

For a H–like atom, $\lambda = 3.0 \times 10^{-8}$ m.

$$\Rightarrow \quad \Delta E_{(2 \to 1)} = 2.18 \times 10^{-18} \times Z^2 \times \left(\frac{1}{1^2} - \frac{1}{2^2}\right) \text{J}$$

$$= E_{\text{Photon}} = \frac{hc}{\lambda} \quad \Rightarrow \quad Z = 2$$

Hence the H–like atom is He^+ ion.

To ionise, He^+ ion, ionisation energy (IE) = –(E_1)

$$IE = -(-13.6 \times 2^2) = +54.4 \text{ eV}$$

The ionisation potential (IP) is the voltage difference required to generate this much energy.

$$\Rightarrow \quad IE = qV = e\,(IP) = 54.4 \text{ eV}$$

$$\Rightarrow \quad IP\,(\text{required}) = 54.4 \text{ Volts}$$

Example - 10 *Match the following :*

	List 1		List 2
(A)	*Orbital angular momentum of the electron in a hydrogen-like atomic orbital*	(p)	*Principal quantum number*
(B)	*A hydrogen-like one-electron wave function obeying Pauli principle*	(q)	*Azimuthal quantum number*
(C)	*Shape, size and orientation of hydrogen-like atomic orbitals*	(r)	*Magnetic quantum number*
(D)	*Probability density of electron at the nucleus in hydrogen-like atom*	(s)	*Electron spin quantum number*

SOLUTION : [A-q, r] [B-p, q, r, s] [C-p, q, r] [D-p, q]

(A) Orbital angular momentum of the electron in a hydrogen like atomic orbital depends on type of atomic orbital (ℓ) and its orientation (m_ℓ).

(B) As per Pauli's principle, every electron is unique, hence all four quantum numbers are required.

(C) Shape, size and orientation of hydrogen-like atomic orbital are indicated by ℓ, n, m_ℓ.

(D) Probability density of electron at the nucleus in hydrogen-like atom is obtained by the square of the wave functions. (ψ^2) and it depends on n and ℓ

Example - 11 *A stationary He^+ ion emits a photon corresponding to the first line (H_α) of Lyman series. The photon thus emitted, strikes a H–atom in the ground state. Find the velocity of the photoelectron ejected out of the hydrogen atom. The value of $R = 1.097 \times 10^7\ m^{-1}$.*

SOLUTION :

The difference in energy (ΔE) will be equal to the energy of the photon emitted.

First line in Lyman series corresponds to the transition $2 \to 1$.

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

$$= 6.54 \times 10^{-18}\ \text{J}$$

The photon of this much energy strikes a H–atom in the ground state. Note that the ionisation energy of H–atom is $+2.18 \times 10^{-18}$ J. This will be the work function of H–atom. Using the Einstein's photoelectric equation :

$$KE = E_i - W_o = \frac{1}{2} m_e v_e^2 \quad [E_i = \text{Incident energy}]$$

$$\Rightarrow \quad v_e = \sqrt{\frac{2(E_i - W_o)}{m_e}}$$

$$\Rightarrow \quad v_e = \sqrt{\frac{2\left(6.54 \times 10^{-18} - 2.18 \times 10^{-18}\right)}{9.1 \times 10^{-31}}}$$

$$\Rightarrow \quad v_e = 3.09 \times 10^6\ \text{m/s}$$

We can also calculate the wavelength of electron ejected out $= 2.36 \times 10^{-10}\ \text{m} \equiv 2.36\ \text{Å}$

$$\lambda_e = \frac{h}{m_e v_e} = \frac{6.626 \times 10^{-34}}{9.1 \times 10^{-31} \times 3.09 \times 10^6}\ \text{m} = 2.36\ \text{Å}$$

Example - 12 *An electron in a hydrogen like species, makes a transition from nth Bohr orbit to next outer Bohr $(\equiv n + 1)$. Find an approximate relation between the dependence of the frequency of the photon absorbed as a function of 'n'. Assume 'n' to be a large value ($n >> 1$).*

SOLUTION :

$$\Delta E_{\substack{(\text{energy difference}) \\ (n \to n+1)}} = h\nu = 2.18 \times 10^{-18} \times Z^2 \left(\frac{1}{n^2} - \frac{1}{(n+1)^2}\right) \text{J}$$

$$\Rightarrow \quad h\nu = 2.18 \times 10^{-18} \times Z^2 \left(\frac{2n+1}{n^2(n+1)^2}\right) \text{J}$$

Since $n >> 1$ (given)

$$\Rightarrow \quad n + 1 \sim n\ ;\ 2n + 1 \approx 2n$$

$$\Rightarrow \quad h\nu \approx 2.18 \times 10^{-18}\ Z^2 \times \frac{2n}{n^4}\ \text{J} \quad \Rightarrow \quad \nu \propto n^{-3}$$