ATOMS

1 THE HYDROGEN ATOM

By the end of nineteenth century most of the efforts of Physicists were directed towards the analysis of the discrete spectrum of radiation emitted when electrical discharges were passed in gases. The hydrogen atom being composed of a nucleus and one electron has the simplest spectrum of all the elements. It was found that various lines in optical and nonoptical regions were systematically spaced in various series. Interestingly it turned out that all the wavelengths of atomic hydrogen were given by a single empirical relation, the Rydberg formula.

$$\frac{1}{\lambda}=R\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right),\ \text{where } R = 1.0967758\times10^{7}\ \text{m}^{-1}$$

where $n_1 = 1$ and $n_2 = 2, 3, 4, \ldots$ gives the Lyman series (ultraviolet region)
$n_1 = 2$ and $n_2 = 3, 4, 5 \ldots$ gives the Balmer series (optical region)
$n_1 = 3$ and $n_2 = 4, 5\ 6, \ldots$ gives the Paschen series (infrared region)
$n_1 = 4$ and $n_2 = 5, 6, 7, \ldots$ gives the Bracket series (for infrared region)
and so on for other series lying in farthest infrared.

The Bohrs theory of hydrogen atom: In 1913 Niels Bohr developed a physical theory of atomic hydrogen from which the Rydberg formula could be derived. Bohr's model for atomic hydrogen is based on certain assumptions, which are as follows:

(i) In the hydrogen atom electron revolves around the nucleus in circular orbits.

(ii) Electron revolves only in those orbits around nucleus where the angular momentum of electron is an integral multiple of $\frac{h}{2\pi}$. These orbits are called stationary orbits. This assumption is called Bohr's quantization rule.

(iii) The energy of electron can take only definite values in a given stationary orbit. The electron can jump from one stationary orbit to other. If it jumps from an orbit of higher energy to an orbit of lower energy it emits a photon of radiation. Similarly an electron can take energy from a source and jumps from a lower energy orbit to a higher energy orbit.

In both the cases energy of radiation involved is given by the Einstein-Planck equation.

$$\Delta E = \frac{hc}{\lambda}$$

Energy of a hydrogen atom: Let the mass of electron be m and it is revolving in an orbit of radius r, then using the quantization rule we get

$$mvr = n\frac{h}{2\pi},\quad \text{where } n \text{ is a positive integer} \qquad \ldots \text{(i)}$$

Also, from the equation of motion of electron we have

$$\frac{Ze^2}{4\pi\varepsilon_0 r^2}=\frac{mv^2}{r} \qquad \ldots \text{(ii)}$$

Though $Z = 1$ for hydrogen, however generally we leave Z in the equation, as the theory is equally applicable to other atoms with all but one of their electrons are removed.

Solving (i) & (ii) we get

$$v = \frac{Ze^2}{2\varepsilon_0 hn} \qquad \ldots \text{(iii)}$$

and $$r = \frac{\varepsilon_0 h^2 n^2}{\pi m Z e^2} \qquad \ldots \text{(iv)}$$

So allowed radii are proportional to n^2. Putting $Z = 1$ and $n = 1$ the quantity $\frac{\varepsilon_0 h^2}{\pi m e^2}$ = 0.53 Å is called **Bohr's radius** and is radius of smallest circle allowed to the electron. Using equation (iii) we write kinetic energy of the electron in n^{th} orbit is

$$K = \frac{1}{2} mv^2 = \frac{mZ^2e^4}{8\varepsilon_0^2h^2n^2} \qquad \dots (v)$$

The potential energy of the atom is

$$U = -\frac{Ze^2}{4\pi\varepsilon_0 r} = -\frac{mZ^2e^4}{4\varepsilon_0^2h^2n^2}$$

So total energy of the atom is

$$E = K + U$$

$$E = -\frac{mZ^2e^4}{8\varepsilon_0^2h^2n^2} \qquad \dots (vi)$$

In deriving the energy of an atom we have considered kinetic energy of electron and potential energy of the electron nucleus pair.

From (vi), the total energy of the atom in the state $n = 1$ is $E_1 = -\frac{mZe^4}{8\varepsilon_0^2h^2}$

For hydrogen atom $Z = 1$ and we get

$E_1 = -13.6$ eV, this is the energy of electron when it moves in the smallest allowed orbit. It is also evident from equation (vi) that energy of the atom in the n^{th} energy state is proportional to $\frac{1}{n^2}$. So we can write.

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

So we get energy in the state $n = 2$ is – 3.4 eV. In the state $n = 3$ it is – 1.5 eV etc. The state of an atom with the lowest energy is called its ground state and states with higher energies are called excited states.

Important results for a hydrogen like atom are

$$V = \frac{Ze^2}{2\varepsilon_0 hn} = \frac{C}{137}\frac{Z}{n}\ \text{m/s} \qquad \dots (1)$$

$$r = \frac{\varepsilon_0 h^2n^2}{\pi mZe^2} = \frac{0.53n^2}{Z}\ \text{Å} \qquad \dots (2)$$

$$E = -\frac{mZ^2e^4}{8\pi\varepsilon_0 h^2n^2} = -\frac{13.6Z^2}{n^2}\ \text{eV} \qquad \dots (3)$$

Hydrogen spectra: Now on the basis of Bohr's model of hydrogen atom it is possible to explain the spectra of hydrogen. If an electron jumps from m^{th} orbit to the n^{th} orbit, the energy of the atom changes from E_m to E_n. The extra energy $E_m - E_n$ is emitted as a photon of electromagnetic radiation. The corresponding wavelength λ is given by

$$\frac{1}{\lambda} = \frac{E_m - E_n}{hc} = \frac{mZ^2e^4}{8\varepsilon_0^2h^3c}\left(\frac{1}{n^2} - \frac{1}{m^2}\right) = RZ^2\left(\frac{1}{n^2} - \frac{1}{m^2}\right) \qquad \dots (4)$$

where $R = \frac{me^4}{8\varepsilon_0^2h^3c}$ is called the Rydberg constant. Putting the values of different constant, the Rydberg constant R comes out to be $1.0973 \times 10^7\ m^{-1}$.

So on the basis of energy levels involved in the transition we can divide the entire hydrogen spectrum in various series.

Lyman series: When an electron jumps from any of the higher states to the ground state ($n = 1$), the series of spectral lines emitted fall in *uv* region and is called as Lyman series. The wavelength λ of any line of the series can be given by

$$\frac{1}{\lambda} = RZ^2\left(\frac{1}{1^2} - \frac{1}{n^2}\right), \qquad n = 2, 3, 4, \dots$$

Balmer series: When an electron makes a transition from any of the higher states to the state with $n = 2$ (first excited state), the series of spectral lines emitted fall in visible region and is called Balmer series. The wavelength of any of Balmer lines is given by

$$\frac{1}{\lambda} = RZ^2\left(\frac{1}{2^2} - \frac{1}{n^2}\right), \qquad n = 3, 4, 5, \ldots$$

Paschen series: When an electron jumps from any of the higher states to the state with $n = 3$ (2nd excited state), the series of spectral lines emitted fall in near infra-red region and is called Paschen series. The wavelength λ for any of the line of Paschen series is given by

$$\frac{1}{\lambda} = RZ^2\left(\frac{1}{3^2} - \frac{1}{n^2}\right), \qquad n = 4, 5, 6, \ldots$$

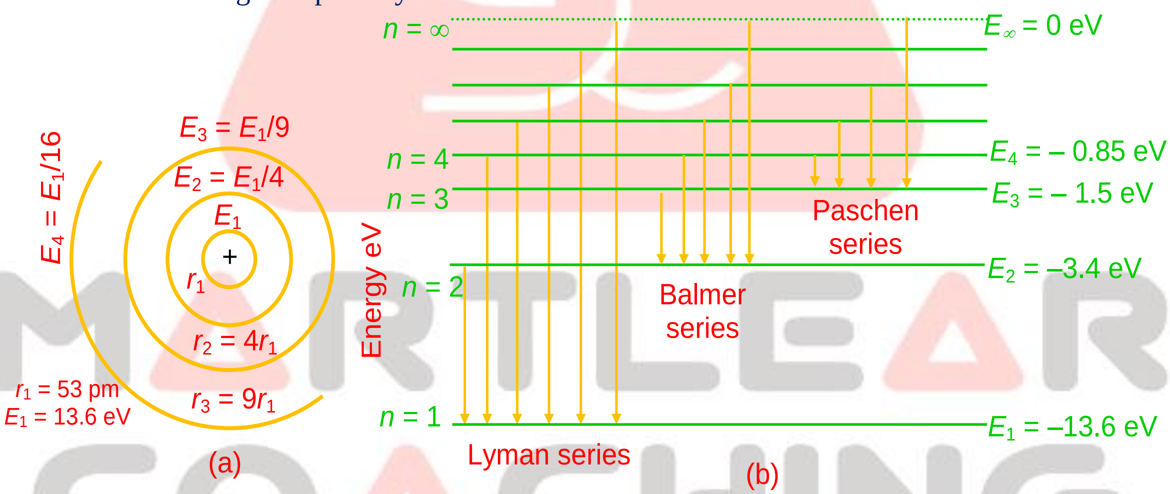
Bracket Series: When an electron jumps from any of the higher states to the state with $n = 4$, (3rd excited state) the series of spectral lines emitted fall in far infrared region and constitute Bracket series. The wavelength λ of any spectral lines of Bracket series is given by

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

Pfund series: Pfund series is constituted by spectral lines emitted when electron jumps from any of the higher energy states to the state with $n = 5$ (4th excited state).

$$\frac{1}{\lambda} = RZ^2\left(\frac{1}{5^2} - \frac{1}{n^2}\right), \qquad n = 6, 7, 8, \ldots$$

Figure below shows schematically the allowed orbits together with the energies of the hydrogen atom. It also shows the allowed energies separately.



Ionization potential: Negative total energy of hydrogen atom mean that hydrogen nucleus and electron constitute a bounded system. Therefore a positive or zero energy of hydrogen atom would mean that electron is not bound to the nucleus i.e., atom is ionised. The minimum energy needed to ionise an atom is called ionisation energy, and the potential difference through which an electron should be accelerated to acquire this energy is called ionisation potential. The ionisation energy of hydrogen atom in ground state is 13.6 eV and ionization potential is 13.6 V.

Binding Energy: Binding energy of a system is defined as energy liberated when its constituents are brought from infinity to form the system. For hydrogen atom binding energy is same as its ionization energy.

Excitation potential: The energy required to take an atom from its ground state to an excited state is called excitation energy of that excited state, and the potential through which the electron should be accelerated to acquire this, is called excitation potential.

2 WAVE PARTICLE DUALITY

Nearly two decades after the 1905 discovery of the particle properties of wave, Louis de-Broglie proposed that moving object have wave as well as particle characteristics. de-Broglie ideas soon received respectful attention despite a complete lack of experimental mandate. The existence of de-Broglie waves was experimentally demonstrated by 1927 and the duality principle they represent provided the starting point for successful development of quantum mechanics.

de-Broglie suggested that a moving body behaves in certain ways as though it has a wave nature. A photon of light of frequency ν has a momentum

$$p = \frac{h\nu}{C} = \frac{h}{\lambda} \quad \text{… (5)}$$

The wavelength of a photon is therefore specified by its momentum as

$$\lambda = \frac{h}{p} \quad \text{… (6)}$$

de-Broglie suggested that equation (6) is a completely general one that applied to material particles as well as photons. The momentum of a particle of mass m and velocity v is $p = mv$, and its de-Broglie wavelength is accordingly.

$$\lambda = \frac{h}{mv} \quad \text{… (7)}$$

The greater the particle's momentum; the shorter is its wavelength. In equation (7) m is the relativistic mass, which is given by

$$m = \frac{m_0}{\sqrt{1 - \frac{v^2}{c^2}}}$$ where m_0 is the rest mass of the particle.

The wave and particle aspects of moving bodies can never be observed at the same time. So one can not ask which is the correct description. All that can be said is that in certain situations a moving body resembles a wave and in others it resembles a particle. Which set of properties is most conspicuous depends on how its de-Broglie wavelength compares with its dimensions and the dimensions of whatever it interacts with.

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