Hydrogen-like ions

The treatment of hydrogen atoms prescribed by Bohr can be generalized to describe the energy level structure and electromagnetic radiation spectra of *hydrogen-like* ions, i.e. a positive nucleus with charge Ze (Z the integer number of protons in the nucleus) orbited by a *single* electron. The nuclear charge comes into the Bohr model in only one place - the Coulomb force acting on the electron, Eq. (3.3), which becomes

$$F = \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r^2} = \frac{m_e v^2}{r}. \quad (3.20)$$

The method applied by Bohr is the same as before, but with e^2 replaced by Ze^2. This results in a new expression for the allowed radii

$$r_n = \frac{4\pi\epsilon_0\hbar^2}{m_e Ze^2}n^2 = \frac{a_0 n^2}{Z}, \quad (3.21)$$

and allowed energy levels

$$E_n = -\frac{m_e(Ze^2)^2}{32\pi^2\epsilon_0^2\hbar^2}\frac{1}{n^2} = -\frac{Z^2e^2}{8\pi\epsilon_0 a_0}\frac{1}{n^2} = -E_1\frac{Z^2}{n^2}. \quad (3.22)$$

The orbits with high-Z atoms are closer to the nucleus and have larger (more negative) energies, i.e. they are more tightly bound to the nucleus. The frequencies of emitted radiation from such an ion will also be modified, and from Eq. (3.22) we see this should scale with Z^2

$$\nu = \frac{E_1 Z^2}{h}\left(\frac{1}{m^2} - \frac{1}{m^2}\right), \quad (3.23)$$

or in terms of wavelength

$$\lambda = \frac{hc}{E_1 Z^2}\left(\frac{1}{m^2} - \frac{1}{m^2}\right)^{-1}. \quad (3.24)$$

Absorption spectra

The Bohr model not only helps us to understand the emission spectrum of atoms, but also explain why atoms do not absorb at all the same wavelengths that it emits. Isolated atoms are normally found in the ground state - excited states live for very short time periods (≈ 1 ns) before decaying to the ground state. The absorption spectrum therefore contains only transitions from the ground state ($n = 1$). To observe transitions from the first excited state ($n = 2$) would require a significant number of atoms to occupy this state initially. Assuming that the atoms are excited by their thermal energies, this implies that to excite an atom to the first excited state from the ground state requires temperature that satisfies

$$k_B T = E_2 - E_1 = 10.2 \text{ eV},$$

which gives a temperature

$$T = \frac{(10.2 \text{ eV})(1.6 \times 10^{-19} \text{ J/eV})}{1.38 \times 10^{-23} \text{ J/K}} \approx 1.2 \times 10^5 \text{ K},$$

which is much larger than room temperature (the surface of the sun has temperature $T \approx 6 \times 10^3$ K).

4.13 PHYSICAL SIGNIFICANCE OF A WAVE FUNCTION [Ψ]

Wave function: *It is the variable quantity that is associated with a moving particle at any position (x, y, z) and at any time 't' and it relates the probability of finding the particle at that point and at that time.*

» It relates the particle and the wave statistically

$$\text{(i.e.,)}\ \Psi(x, y, z, t) = A\, e^{-i\omega(t - x/v)}$$

$$\boxed{\text{(or)}\ \Psi = \psi\, e^{-i\omega t}}$$

» Wave function gives the information about the particle behaviour.

» Ψ is a complex quantity and individually it does not have any meaning.

» $|\Psi|^2 = \Psi^* \Psi$ is real and positive, it has physical meaning. This concept is similar to light. In light, amplitude may be positive (or) negative but the Intensity, which is the square of amplitude is real and is measurable.

» $|\Psi|^2$ represents the probability density (or) probability of finding the particle per unit volume.

» For a given volume $d\tau$, the probability of finding the particle is given by

$$\text{Probability } (P) = \iiint |\Psi|^2\, d\tau$$

where $d\tau = dx \cdot dy \cdot dz$

- The probability will have any value between zero to one. (i.e.,)
  (i) If $P = 0$ then there is no chance for finding the particle (i.e.,) there is no particle, within the given limits.
  (ii) If $P = 1$ then there is 100% chance for finding the particle (i.e.,) the particle is definitely present, within the given limits.
  (iii) If $P = 0.7$, then there is 70% chance for finding the particle and 30% there is no chance for finding the particle, within the given limits.

xample: If a particle is definitely present within a one dimensional box (x-direction) f length 'l', then the probability of finding the particle can be written as

$$P = \int_0^l |\Psi|^2 dx = 1$$

DUAL NATURE OF RADIATION

de-Broglie concept of Dual Nature

The universe is made of Radiation (light) and matter (particles). The light exhibits the dual nature (i.e.,) it can behaves both as a wave (Interference, diffraction phenomenon) and as a particle (Compton effect, photo-electric effect etc).

Since the nature loves symmetry, in 1924 Louis de-Broglie suggested that an electron (or) any other material particle must exhibit wave like properties in addition to particle nature.

The waves associated with a material particle are called as ***Matter waves***

de-Broglie Wavelength

From the theory of light, considering a photon as a particle the total energy of the photon is given by $E = mc^2$. ... (1)

where $m \rightarrow$ Mass of the particle

$c \rightarrow$ Velocity of light

Considering the photon as a wave, the total energy is given by $E = h\nu$ ... (2)

where $h \rightarrow$ Planck's constant

$\nu \rightarrow$ Frequency of radiation

From equations (1) and (2) we can write $E = mc^2 = h\nu$ ... (3)

We know momentum = mass × velocity

$$p = mc$$

$$p = \frac{h\nu}{c}$$

Since $\frac{c}{\nu} = \lambda$ we can write $p = \frac{h}{\lambda}$

(or) The wavelength of a photon $\lambda = \frac{h}{p}$ ... (

de-Broglie suggested that equation (4) can be applied both for photons ar material particles. If m is the mass of the particle and v is the velocity of th particle, then

Momentum $p = mv$.

$$\therefore \text{de-Broglie wavelength } \lambda = \frac{h}{mv} \quad \text{... (5)}$$

WAVE PROPERTIES OF MATTER: de-BROGLIE WAVELENGTH

In 1925, de-Broglie made a suggestion that a moving particle, whatever its nature, has wave properties associated with it and its wavelength is given by

$$\lambda = h/mv = h/p$$

where h is Planck's constant, m is the mass and v is the velocity of the particle with which it is moving. This equation is known as de-Broglie relation

or $$mv = h/\lambda$$

which states that "the momentum of a moving particle is inversely proportional to the wave length of the wave associated with it."

As the photon travels in free space with velocity of light, c, its momentum is given by

$$p = mc = mc^2/c = E/c = h\nu/c = h/\lambda$$

or

$$\lambda = h/p$$

de-Broglie assumed that this equation should be equally applicable to both the photons of radiation and material particles like electrons. Hence, if m is the mass of the particle moving with velocity v, then its momentum $p = mv$. The wavelength of the wave associated with material particle is

$$\lambda = h/mv$$

This equation is known as de-Broglie wave equation and λ called de-Broglie wavelength. Some of de Broglie's ideas were used by Schrodinger, Dirac, Born, Heisenberg and other physicists which developed into the modem theory of Quantum mechanics.

GROUP VELOCITY AND PHASE VELOCITY: -

(A WAVE PACKET) A particle while moving with a velocity v can-be explained as a group of waves which is moving in one direction. The group velocity of these waves can be shown to be equal to the velocity of the particle.

The velocity of the propagation of the wave, called phase velocity , v_p is given by $\nu.\lambda$

The simplest plane monochromatic wave expressed as exp[$i(kx- \omega t)$]

Where $\omega = 2\pi\nu$ and wavelength $\lambda=2\pi/k$ travelling in the direction of its wave vector $k$with constant velocity $v_p = \omega/k$

According to de Broglie hypothesis a material particle in motion is associated with a wave of wave length $\lambda = h/mv$, where m is the mass and v the velocity of the particle. If E is the energy of the particle and υ the frequency of the wave then by quantum condition

$$E = h\upsilon \quad or \quad \upsilon = E/h$$

But according to Einstein's mass energy relation we have

$$E = mc^2, \text{ so that } \upsilon = mc^2/h$$

Also $\quad E = h\upsilon = h\omega/2\pi = \hbar\omega \quad where\ h/2\pi = \hbar$

And from de-Broglie relation, the momentum, p and wave number k are related as

$$p = \hbar k \quad (as\ p = h/\lambda = \hbar 2\pi/\lambda = \hbar k)$$

A wave packet consists of a group of waves, each having slightly different velocity and wavelength. Such a packet moves with its own velocity v_g called the group velocity. The group velocity may be defined as ***"the velocity with which a slowly varying envelope or packet due to a group of waves travels in a medium."*** This is the velocity with which the energy in the wave group is transmitted.

A wave packet can be made by superposition of waves and can be written as

$$\Psi = a_1\psi_1 + a_2\psi_2 + \ldots$$

Mathematically it can be shown that such envelope of waves propagate with the velocity

$$v_g = d\omega/dk$$

v_g is known as *the group velocity* of the wave since it represents the velocity of motion of a group of waves, which make up the wave packet.

$$\omega = 2\pi v \text{ and } k = 2\pi/\lambda \text{ or } d\omega = (2\pi\ dv) \text{ and } dk = (-2\pi/\lambda^2)d\lambda$$

then $$v_g = d\omega/dk = (2\pi\ dv)/(-2\pi/\lambda^2)d\lambda = -\lambda^2\, dv/d\lambda.$$