School of Basic and Applied Science

Curse Code :MSCP 6002 Curse Name: ATOMIC AND MOLECULAR PHYSICS

Unit – 1: Atomic Spectra

CO1: Apply the concept of spin and orbit interaction to explain the atomic spectra

Contents:

Atomic and Molecular spectroscopy
Bohr Postulates
BOHR THEORY OF HYDROGEN ATOMS
Motion of electron in Orbit
Bohr radius
Velocity of electron in Orbit
Kinetic energy, potentials energy and total energy
Rydberg's Contacts and Rydberg's Equation

Name of the Faculty: Dr. Anis Ahmad Program Name: M.Sc. Physics

Atomic and Molecular spectroscopy

Hydrogen Atom

The nuclear model of the atom had been proposed by Rutherford in 1911. The model pictures the atom as a heavy, positively-charged nucleus, around which the much lighter, negatively-charged electrons circulate, much like planets in the Solar system. This model is however completely untenable from the standpoint of classical electromagnetic theory, for an accelerating electron (orbital motion represents an acceleration) should radiate away its energy. In fact, a hydrogen atom should exist for no longer than 10^{-10} sec. This is one of the worst quanti-tative predictions in the history of physics.

Bohr sought to avoid an atomic catastrophe by proposing that certain orbits of the electron around the nucleus could be exempted from classical electrodynamics and remain stable. The Bohr model was quantitatively successful for the hydrogen atom, as we shall now show.

Atomic and Molecular spectroscopy

Spectroscopy is the branch of physics which deals with the observation & interpretation of radiation emitted and observed by atoms and molecules. It provides information about the arrangement and motion of the outer electrons (optical spectroscopy), about inner electrons (X- rays spectroscopy), about angular momentum , magnetic moment, distribution of charges and magnetism of the nucleus . since $\upsilon = c/\lambda$, the frequency of monochromatic EM wave does not alter in different medium. so, for analysis of spectral lines, frequency is more fundamental than wavelength. but frequency is very large for visible light.

Thus in spectroscopy 'wave number'(the number of waves per meter or per cm) are usually used

the wave number $\bar{\nu} = \frac{1}{\text{wave length}}$ i.e wave number is reciprocal of wavelength in vacuum and it is expressed in cm^{-1} or m^{-1}.

Bohr's Postulates

Niels Bohr, in 1913, developed a model of atomic structure which was in accurate quantitative agreement with the observed hydrogen and hydrogen-like spectra. This model is based on certain postulates which are :

(i) ***An electron in an atom moves in a circular orbit about the nucleus under the influence of the Coulomb attraction between the electron and the nucleus, according to the laws of classical mechanics.***

This postulate bases Bohr's model on the existence of the atomic nucleus and embodies some of the ideas concerning the stability of the nuclear atom.

(ii) ***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 $h/2\pi$, where h is Planck's constant.*** That is,

$$|\vec{L}| = \frac{nh}{2\pi}; \quad n = 1, 2, 3, \ldots\ldots$$

This postulate introduces quantisation. We shall see that the quantisation of the orbital angular momentum of the atomic electron leads to the quantisation of its total energy.

(iii) ***The electron, in spite of its accelerated motion, does not radiate electromagnetic energy while moving in an allowed orbit.*** Thus, its total energy remains stationary.

This postulate removes the problem of the stability of the electron moving in a circular orbit, due to the emission of electromagnetic energy as demanded by classical theory.

(iv) ***Electromagnetic radiation is emitted if an electron, initially moving in an orbit of total energy E_i, discontinuously changes its motion so that it moves in a lower orbit of total energy E_f.*** The frequency ν' of the emitted radiation is given by

$$\nu' = \frac{E_i - E_f}{h}.$$

BOHR THEORY OF HYDROGEN ATOMS

When atomic gas or vapor is excited, the emitted radiations after being dispersed by a suitable spectrometer becomes concentrated at a number of discreate wavelenght. Each of these wavelength components is called a **'spectral line'** and whole family of lines is called **"line spectrum" or 'atomic spectrum'**. Each atom has its own characteristics spectrum this makes spectroscopy as useful tool for chemical analysis of unknown substance.

Bohr Postulates

(i) Electron revolve around nucleus under Coulomb force of attraction.

(ii) Out of infinite number of orbitals, it is only possible for an electron to move in an orbit for which the magnitude of its orbital angular momentum L is an integral multiple of h/ 2π.

i.e**. L= n h/ 2π.,** where n=1,2,3,4, 5……………………….

this postulate introduces the quantization of total energy of electron.

(i) Circularly moving electron does not radiate energy

(ii) So, the frequency of radiated energy stable (constant) due to transition from higher energy level to lower energy level. it is

$$\upsilon = (E_2 - E_1) / h$$

this theory mix up the classical and non-classical theory

Classical theory: Circular motion, Coulomb law

Non- Classical Theory: Quantization of orbital angular momentum, Radiation properties of accelerated electron

BOHR THEORY OF HYDROGEN ATOM: -

Assume electron of mas 'm' charge 'e' is revolving in circular orbit of radius 'r' w.r.to. nucleus of charge 'ze' for hydrogen atom Z=1

Assume that nucleus is infinitely heavy compared to the electron , hence nucleus remains fixed in the space,

From Coulombic force of Attraction

Where $Fe=(1/4\pi\epsilon_0)Ze.e/r^2$ coulombic force of attraction and

$Fc= mv^2/r$, centripetal force

Therefore, Fe= Fc

The condition for mechanical stability of the electron is

$(1/4\pi\epsilon_0)Ze.e/r^2= mv^2/r$ As we know $Fe= (1/4\pi\epsilon_0)q1.q2/r^2$

$r= (1/4\pi\epsilon_0)Ze.e/ mv^2$ (1)

Bohr's Radius:

From Bohr quantization of angular momentum

$L= mvr= nh/2\pi$ (2)

$v= (nh/2\pi mr)$ (3)

$v^2= (nh/2\pi mr)^2$ (3)

from (1) and (3) we have

$r_n= n^2h^2\epsilon_0/\pi mZe^2$ This may be written as $r_n= \{h^2\epsilon_0/\pi me^2\}\{n^2/Z\}$ (4)

the radii of circular orbit are proportional to n^2, for hydrogen atom , Z=1 and for first orbit n=1, then $r=0.529A^0$ Approximately $r=0.53A^0$

$r=0.53A^0$. which is known as **Bohr Radius of Hydrogen atom.**

Now, putting the value of (4) in (3) we have

$v_n= \{e^2/2h\epsilon_0\}\{Z/n\}$, which is the orbital velocity of electron in the hydrogen atom (for, Z=1 and n=1)

$v= 2.18\times10^6$m/s (less than 1% of c) i.e c /137 , where $c=3\times 10^8$ m/s

classical approach is used (not relativistic)

But for Larger value of Z, v becomes relativistic.

Total Energy

Total energy = KE+ PE

$KE= mv^2/2 = Ze^2/8\pi\epsilon_0 r$

and $PE= -Ze^2/4\pi\epsilon_0 r$

Therefore, total Energy

$E= -Ze^2/8\pi\epsilon_0 r$ (6)

Putting the value of r from (4) in (6) we have

$E_n=-mZ^2e^4/8\epsilon_0^2h^2n^2$, this imply that $E_n= - \{me^4/8\epsilon_0^2h^2\} \{Z^2/n^2\}$

$E_n \propto 1/n^2$

So quantization of orbital angular momentum of the electron leads to quantization of its total energy.

Therefore, E1=-13.6 eV, E2= -3.39eV, …. etc.

The ground state energy of hydrogen atom is a convenient energy unit . it is called Rydberg&

I Rydberg= 13.6eV

To remove the electron from its ground state n=1 to infinity, a minimum of 13.6eV of energy is required. Thus, 13.6eV is the binding energy of electron for Hydrogen atom.

The binding energy (ionization energy) is numerically equal to the energy of the ground state of the atom

Term Value: The energy values of the various quantum numbers states divided by (-hc) are called term value of the state.

So, $T_n = E_n/-hc = mZ^2e^4/8\epsilon_0^2h^2n^2\,(hc)$

$$T_n = mZ^2e^4/8\epsilon_0^2h^3n^2c \qquad (7)$$

The quantity "$me^4/8\epsilon_0^2h^3c$" is called as Rydberg's Constant & denoted as R_∞ for infinitely heavy nucleus

Since, $R_\infty = me^4/8\epsilon_0^2h^3c$

Therefore, $T_n = R_\infty Z^2/n^2 \qquad (8)$

i.e lowest and the most stable energy level has the largest Term value.

Origin of One Electron (Hydrogen Like) Spectra: -

Energy of a quantum state can be given in terms of R_∞ as

$E_n = -R_\infty Z^2 hc / n^2$ (9)

the frequency υ emitted by electron initially moving in n_2 orbital and drops to a lower orbit of quantum number n_1

then, $\upsilon = (E_1 - E_2) / h$

$\upsilon = = R_\infty Z^2 c / (n_1^2 - n_2^2)$

$\upsilon / c = R_\infty Z^2 / (n_1^2 - n_2^2)$

$$\text{wavenumber} = \bar{\nu} = \frac{1}{\lambda} = RZ^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$\text{Energy} = E = hc\bar{\nu} = hcRZ^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

Therefore, Wave number = $R_\infty Z^2 / (1/n_1^2 - 1/n_2^2)$ (10)

When atoms receive energy from out side the electron makes transition from lower state to higher state. after short intervalof time, the atom emits the excess energy and return to its ground state.

This is accomplished by a series of transition in which electron drops successively lower energy state.

Examples: if electron is excited to the n=7 and drops through state n=4 & n=3 to ground atate n-1. Then three lines are emitted and corresponding wave number can be calculated using equation (10) (i) for n_2 =7 & n_1= 4, (ii) n_2=4 and n_1=3 (iii) n_1=3 and n_2=1.

For hydrogen Atom Z=1 and

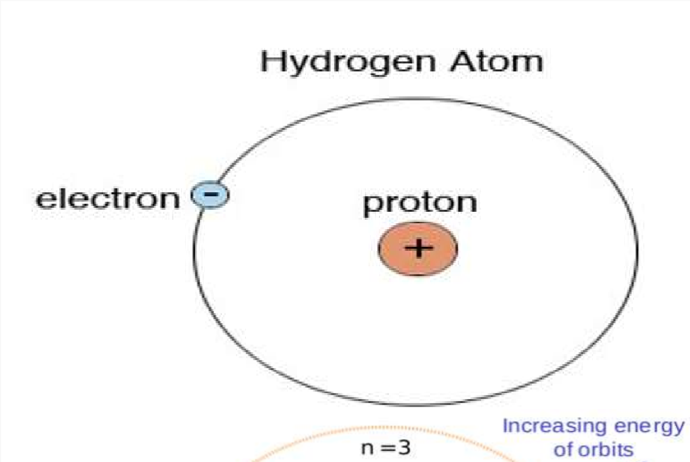
Wave number = R_∞ $(1/nf^2-1/ni^2)$

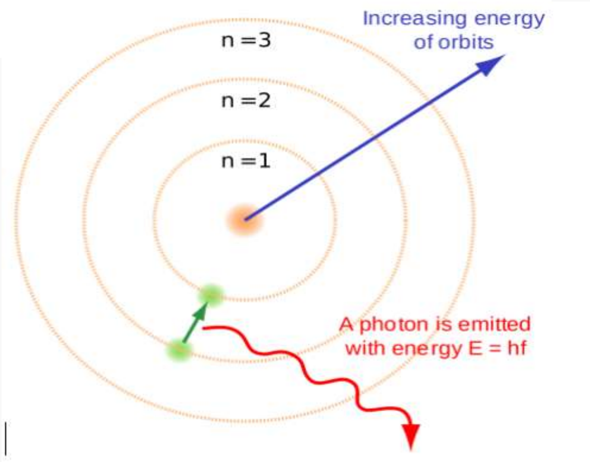
It is identical with formula for various series the hydrogen spectrum if $R_\infty = R_H$

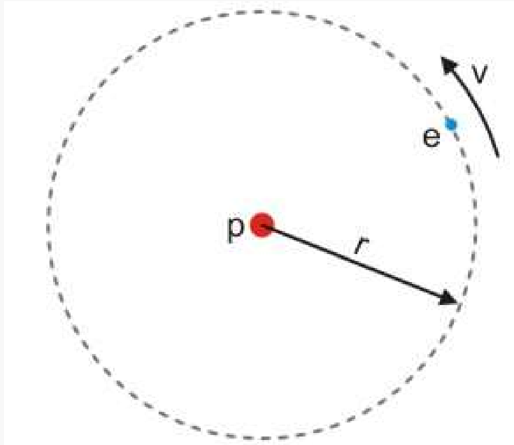
According to the Bohr model $R_\infty = me^4/8\epsilon_0^2h^3c = 1.0973x10^7/$ m.

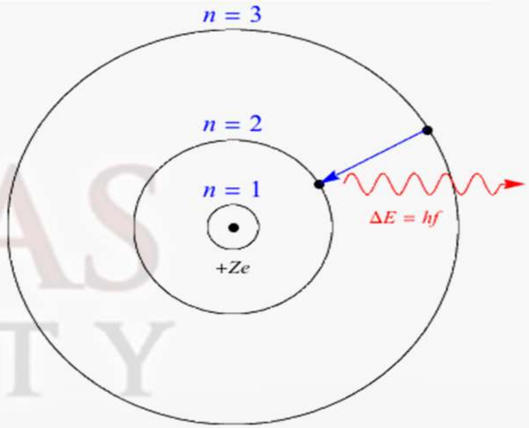
Various line spectra are obtained for the transition of electron from a state to a final state.

Hydrogen Atom









Summary : Hydrogen Atom

Niels Bohr proposed that

In an atom, electrons (negatively charged) revolve around the positively charged nucleus (fixed) in a definite circular path called as orbits or shells without collapsing.

The angular momentum, L , of the orbiting electron is a positive integer multiple of h/2π , which often is written as $\hbar$ and called h-bar. $L=n\hbar$ where n=1,2,3,…

These orbits have discrete energies and radiation is emitted at a discrete frequency when the electron makes a transition from one orbit to another.

The energy difference between the orbits is proportional to the frequency of radiation emitted $E_f - E_i = h\nu$

where the constant of proportionality, h, is Planck's constant.

$E_f - E_i$ is the difference between energy levels and $h\nu$ is the energy of the emitted photon.

Bohr's revolutionary proposal was taken seriously because with these ideas, he could derive Rydberg's formula and calculate a value for the Rydberg constant.

References:

1. Raj Kumar, Atomic and Molecular Spectra: Laser, Kedear Nath Publication, Meerut, 2015
2. Arthur Beiser, Concepts of Modern Physics, 6th ed.,McGraw Hill, New Delhi, 2008.
3. Harvey Elliott White, Introduction to Atomic Spectra, McGraw Hill, 1963.
4. G M Barrow, Introduction to molecular spectroscopy, Tata McGraw Hill,Japan, 1962.
5. Internet