Department of Mathematics and Natural Sciences

CHE101: Lecture 03

Contents:

- Spectrum
- Quantum Theory of Energy
- Bohr's atomic theory
- Duality of electron
- Schrodinger's equation
- Quantum Number

Quantum Theory Of Radiation

- When atoms or molecules absorb or emit radiant energy, they do so in separate 'units of waves' called quanta or photons.
- Thus light radiations obtained from energised or 'excited atoms' consist of a stream of photons and not continuous waves.
- The energy, E, of a quantum or photon is given by the relation **$E = h\nu$**
- An atom or molecule can emit (or absorb) either one quantum of energy ($h\nu$) or any whole number multiple of this unit.

Mathematical Problem

- Calculate the magnitude of the energy of the photon (or quantum) associated with light of wavelength 6057.8 Å. (Å = 10^{-8} cm)

Photoelectric Effect

- When a beam of light of sufficiently high frequency is allowed to strike a metal surface in vacuum, electrons are ejected from the metal surface.

Observations:

- An increase in the intensity of incident light does not increase the energy of the photoelectrons. It merely increases their rate of emission.

- The kinetic energy of the photoelectrons increases linearly with the frequency of the incident light.

- If the frequency is decreased below a certain critical value (Threshold frequency, ν_0), no electrons are ejected at all.

The Classical Physics

- predicts that the kinetic energy of the photoelectrons should depend on the intensity of light and not on the frequency.
- Thus it fails to explain the above observations.

Einstein's Explanation Of Photoelectric Effect

- interpreted the Photoelectric effect by application of the Quantum theory of light
- A photon of incident light transmits its energy (hv) to an electron in the metal surface which escapes with kinetic energy $\frac{1}{2}mv^2$.

- The greater intensity of incident light merely implies greater number of photons each of which releases one electron. This increases the rate of emission of electrons, while the kinetic energy of individual photons remains unaffected.

Einstein's Explanation Of Photoelectric Effect

- To release an electron from the metal surface, the incident photon has first to overcome the attractive force exerted by the positive ion of the metal.
- The energy of a photon ($h\nu$) is proportional to the frequency of incident light.
- The frequency which provides enough energy just to release the electron from the metal surface, will be the threshold frequency, ν_0.

Einstein's Explanation Of Photoelectric Effect

- For frequency less than v_0, no electrons will be emitted.
- For higher frequencies v > v0, a part of the energy goes to loosen the electron and remaining for imparting kinetic energy to the photoelectron.
- Thus, $hv = hv_0 + \frac{1}{2} mv^2$

hv = the energy of the incoming photon

Hv_0 = the minimum energy for an electron to escape from the metal

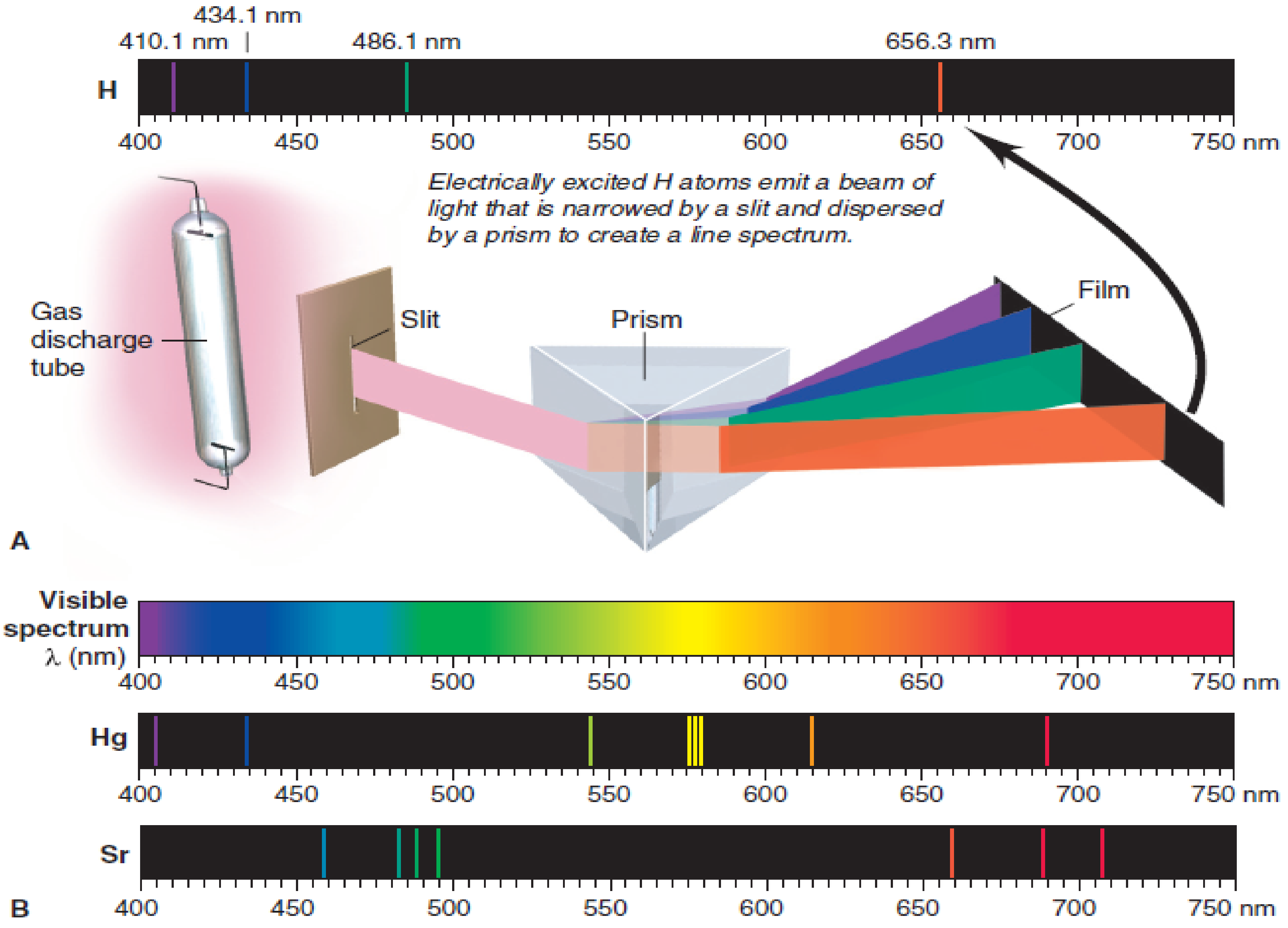
$\frac{1}{2} mv^2$ = is the kinetic energy of the photoelectron.

- hv_0 is constant for a particular solid and is designated as W, the work function.

Mathematical Problems

- What is the minimum energy that photons must possess in order to produce photoelectric effect with platinum metal? The threshold frequency for platinum is 1.3×10^{15} sec^{-1}.

- Calculate the kinetic energy of an electron emitted from a surface of potassium metal (work function = 3.62×10^{-12} erg) by light of wavelength 5.5×10^{-8} cm.


434.1 nm
410.1 nm
486.1 nm
656.3 nm
H
400
450
500
550
600
650
700
750 nm
Electrically excited H atoms emit a beam of light that is narrowed by a slit and dispersed by a prism to create a line spectrum.
Gas discharge tube
Slit
Prism
Film
A
Visible spectrum
λ (nm)
400
450
500
550
600
650
700
750 nm
Hg
400
450
500
550
600
650
700
750 nm
Sr
B
400
450
500
550
600
650
700
750 nm

Absorption spectrum:

- When white light is passed through a substance, black lines appear in the spectrum where light of some wavelengths have been absorbed by the substance.
- The pattern of frequencies absorbed by the substance is called absorption spectrum.
- From the absorption spectrum we get dark lines.

Emission spectrum:

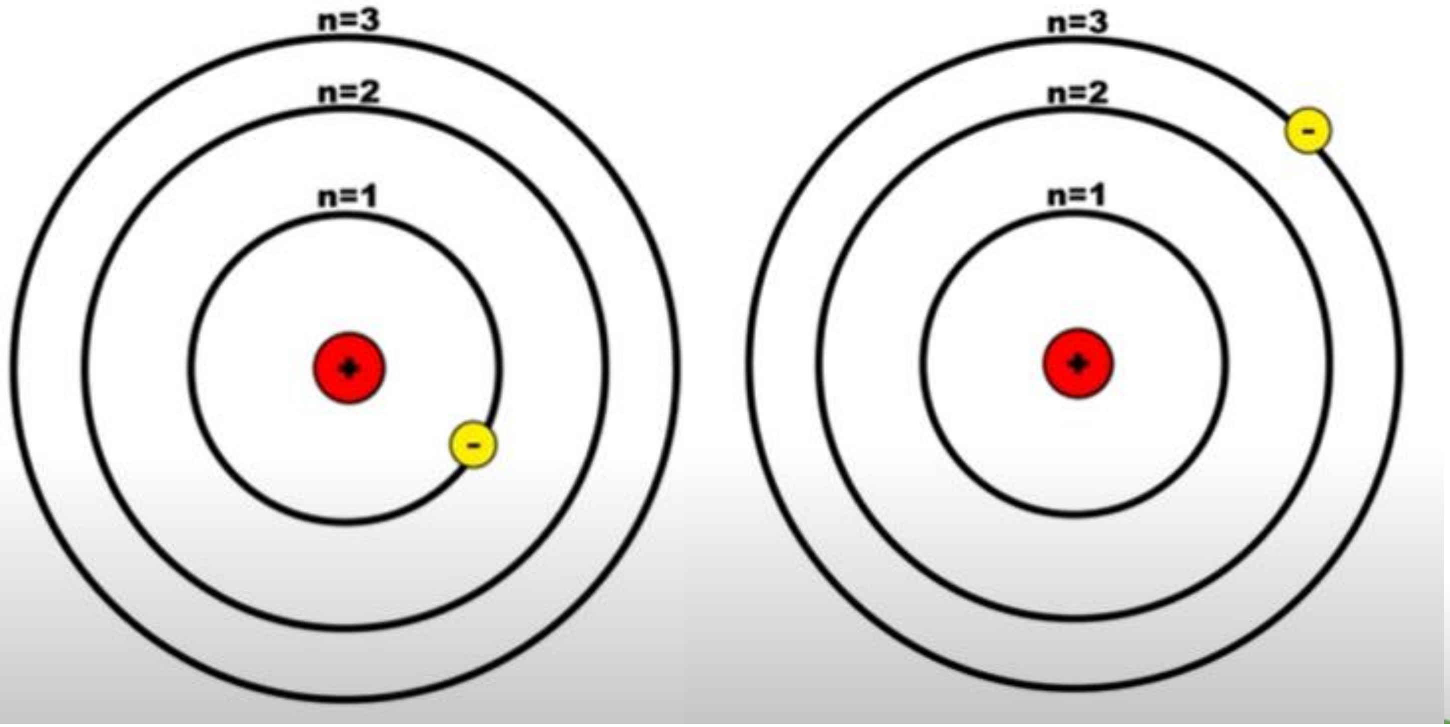
- If atoms or molecules are heated to sufficiently high temperature, they emit light of certain wavelengths.
- The pattern of frequencies emitted by the substance is called emission spectrum.
- From the emission spectrum we get bright lines.

Q: How is a bright line spectrum produced?

- When electrons jump from the excited state to the ground state, the electrons emit energy in the form of light, producing a bright-line spectrum.
- Each element has its own unique bright-line spectrum.

Q: Is the spectrum for the incandescent light a continuous spectrum or a line spectrum?

- Incandescent bulb is equivalent to white light, i.e it has all the seven wavelengths of light.
- Therefore when passed through a prism it is disperses into all the seven wavelengths without any spaces or boundaries and is obtained on the screen as a continuous spectrum.



$\Delta E_{electron} = E_{photon}$

Rydberg Constant, $R_H = 2.18 \times 10^{-18}$ J

$$\Delta E_{electron} = -R_H\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

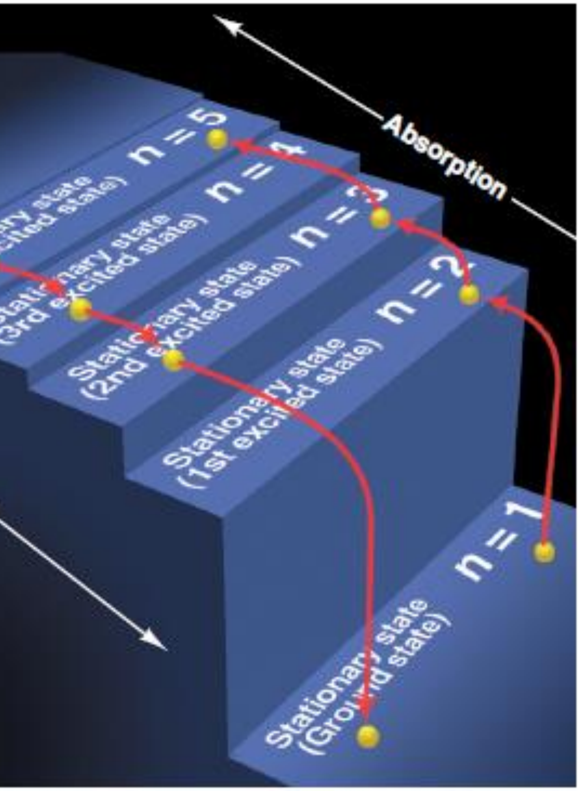
where the electron ends up

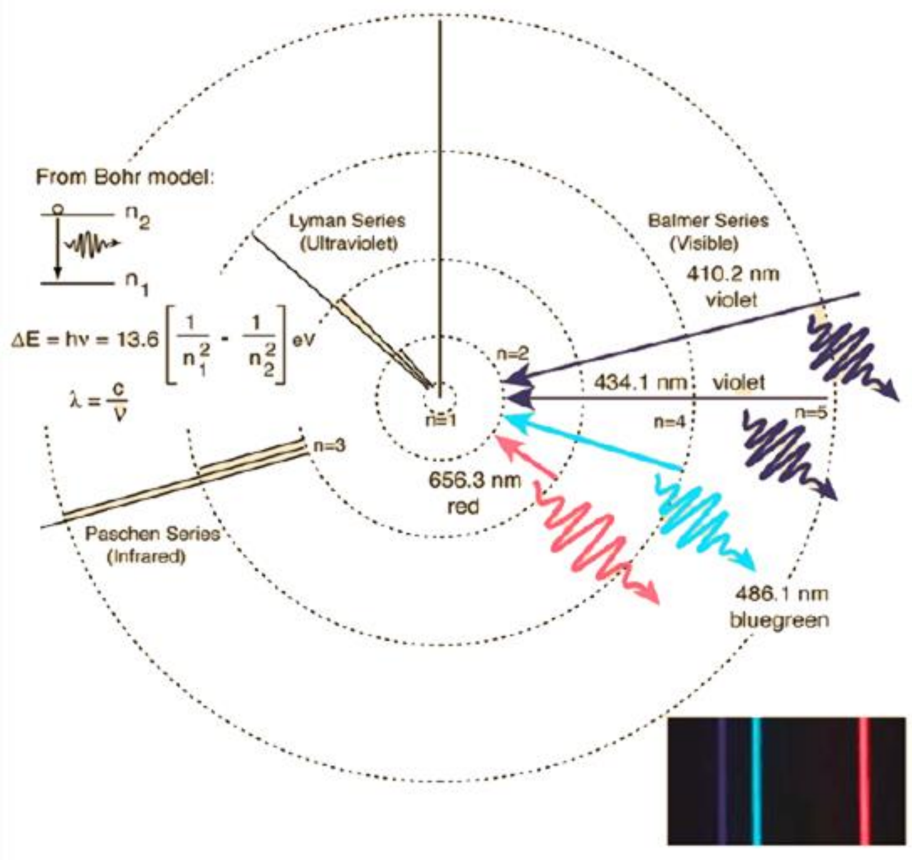
where the electron begins

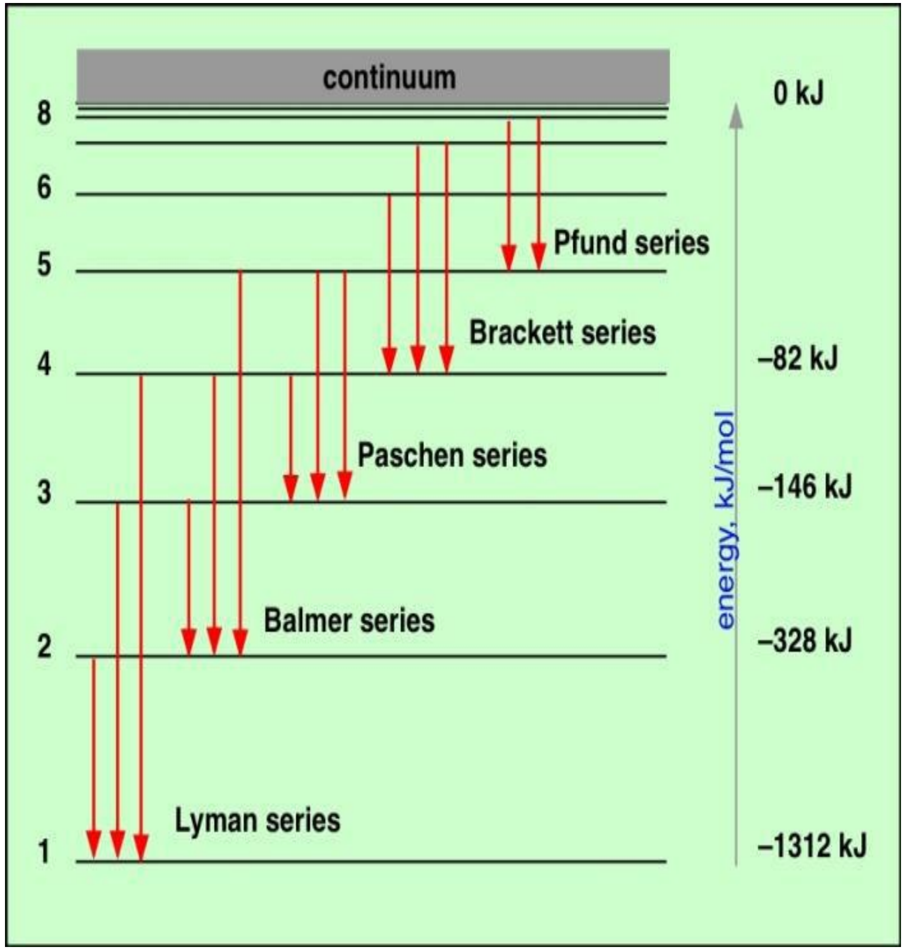
- When the atom emits energy, the electron moves closer to the nucleus ($n_{final} < n_{initial}$), so the atom's final energy is a larger negative number and ΔE is negative.

- When the atom absorbs energy, the electron moves away from the nucleus ($n_{final} > n_{initial}$), so the atom's final energy is a smaller negative number and ΔE is positive.

H-atom spectrum







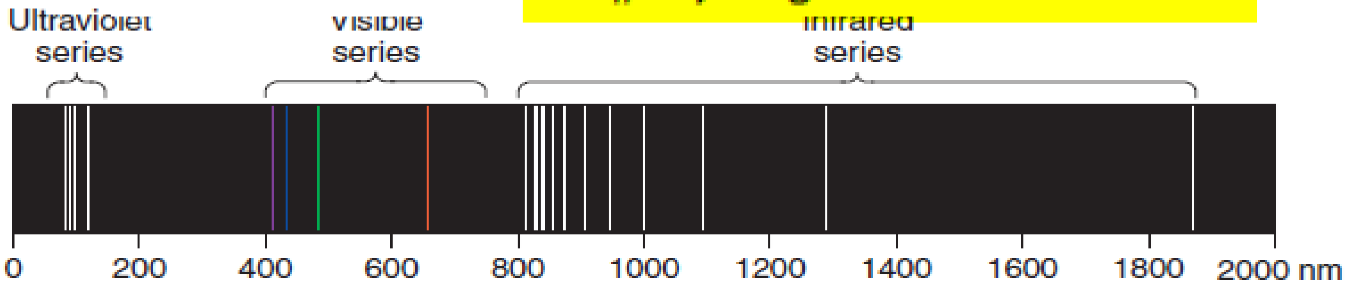
$$|\Delta E| = h\nu = \frac{hc}{\lambda} \quad \text{or} \quad \lambda = \frac{hc}{|\Delta E|}$$

Planck's constant, h= 6.626 x 10 $^{-34}$ Js

Since these transitions result in the emission of a photon of frequency ν and energy h ν, we can write-

$$\frac{1}{\lambda} = R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \text{ where } n_i > n_f$$

$R = R_H$ = Rydberg constant = 109737 cm^{-1}



Series	Region of spectrum	Equation for wavenumber($\bar{\nu}$)
Lyman series	Ultraviolet	$\bar{\nu} = R_H\left(\frac{1}{1^2} - \frac{1}{n^2}\right)$, n =2,3,4,5...
Balmer series	Visible/ultraviolet	$\bar{\nu} = R_H\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$, n =3,4,5,6..
Paschen series	Infrared	$\bar{\nu} = R_H\left(\frac{1}{3^2} - \frac{1}{n^2}\right)$, n =4,5,6,7...
Breckett series	Infrared	$\bar{\nu} = R_H\left(\frac{1}{4^2} - \frac{1}{n^2}\right)$, n =5,6,7,8...
Pfund series	Infrared	$\bar{\nu} = R_H\left(\frac{1}{5^2} - \frac{1}{n^2}\right)$, n =6,7,8...

- If an electron jumps from the 4th orbit to the 2nd orbit, how much energy would it absorb or emit?
- Also determine the wavelength of the emitted photon.

Postulates of Bohr's Theory

Postulates of Energy Levels

1. **Electrons travel around the nucleus in specific permitted circular orbits and in no others**

- Electrons in each orbit have a definite energy and are at a fixed distance from the nucleus.
- The orbits are given the letter designation n and each is numbered 1, 2, 3, etc. (or K, L, M, etc.) as the distance from the nucleus increases.

2. **While in these specific orbits, an electron does not radiate (or lose) energy:**

- in each of these orbits the energy of an electron remains the same i.e. it neither loses nor gains energy.
- Hence the specific orbits available to the electron in an atom are referred to as stationary energy levels or simply energy levels

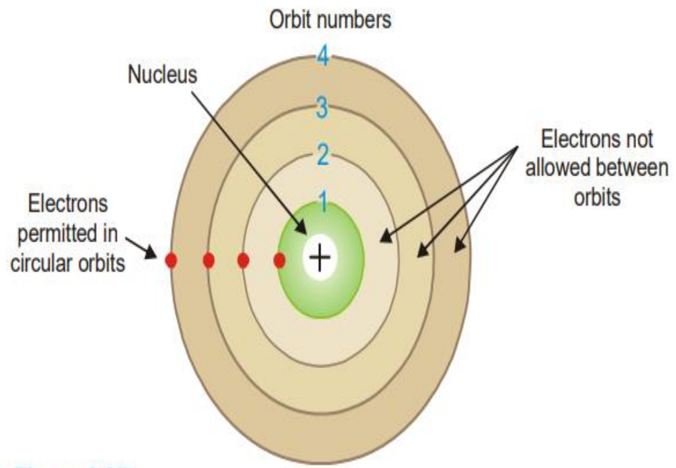


Figure 1.25
Circular electron orbits or stationary energy levels in an atom.

Postulates of Bohr's Theory

Postulates of Energy Levels

3. An electron can move from one energy level to another by quantum or photon jumps only.

- The quantum or photon of energy absorbed or emitted is the difference between the lower and higher energy levels of the atom

$$\Delta E = E_{high} - E_{low} = hv$$

4. The angular momentum (mvr) of an electron orbiting around the nucleus is an integral multiple of Planck's constant divided by 2π.

- Angular momentum = $mvr = n\,(h/2\pi)$

Calculation of radius of orbits

Consider an electron of charge e revolving around a nucleus of charge Ze, where Z is the atomic number and e the charge on a proton. Let m be the mass of the electron, r the radius of the orbit and v the tangential velocity of the revolving electron.

The electrostatic force of attraction between the nucleus and the electron (Coulomb's law),

$$= \frac{Ze \times e}{r^2}$$

The centrifugal force acting on the electron

$$= \frac{mv^2}{r}$$

Bohr assumed that these two opposing forces must be balancing each other exactly to keep the electron in orbit. Thus,

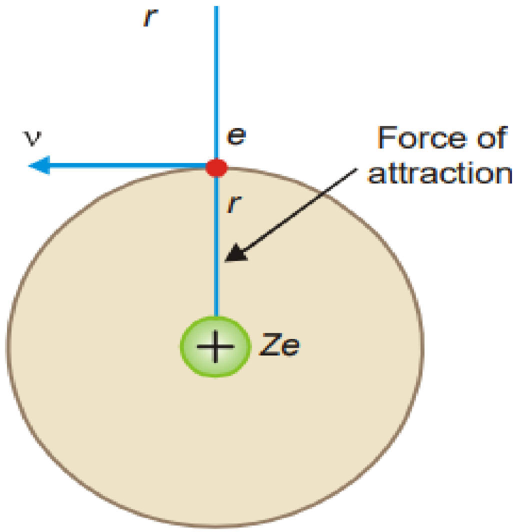
$$\frac{Ze^2}{r^2} = \frac{mv^2}{r}$$

For hydrogen $Z = 1$, therefore,

$$\frac{e^2}{r^2} = \frac{mv^2}{r} \qquad ...(1)$$

Multiplying both sides by r

$$\frac{e^2}{r} = mv^2 \qquad ...(2)$$



■ **Figure 1.27**
Forces keeping electron in orbit.

Calculation of radius of orbits

According to one of the postulates of Bohr's theory, angular momentum of the revolving electron is given by the expression

$$mvr = \frac{nh}{2\pi}$$

or
$$\nu = \frac{nh}{2\pi\ mr} \qquad ...(3)$$

Substituting the value of ν in equation (2),

$$\frac{e^2}{r} = m\left(\frac{nh}{2\pi\ mr}\right)^2$$

Solving for r,

$$r = \frac{n^2 h^2}{4\pi^2\ me^2} \qquad ...(4)$$

Since the value of h, m and e had been determined experimentally, substituting these values in (4), we have

$$r = n^2 \times 0.529 \times 10^{-8}\ \text{cm} \qquad ...(5)$$

where n is the principal quantum number and hence the number of the orbit.

When $n = 1$, the equation (5) becomes

$$r = 0.529 \times 10^{-8}\ \text{cm} = \alpha_0 \qquad ...(6)$$

This last quantity, α_0 called the first **Bohr radius** was taken by Bohr to be the radius of the hydrogen atom in the ground state. This value is reasonably consistent with other information on the size of atoms. When $n = 2, 3, 4$ etc., the value of the second and third orbits of hydrogen comprising the electron in the excited state can be calculated.

Energy of electron in each orbit

For hydrogen atom, the energy of the revolving electron, E is the sum of its kinetic energy $\left(\frac{1}{2}mv^2\right)$ and potential energy $\left(-\frac{e^2}{r}\right)$.

$$E = \frac{1}{2}mv^2 - \frac{e^2}{r} \qquad ...(7)$$

From equation (1)

$$mv^2 = \frac{e^2}{r}$$

Substituting the value of mv^2 in (7)

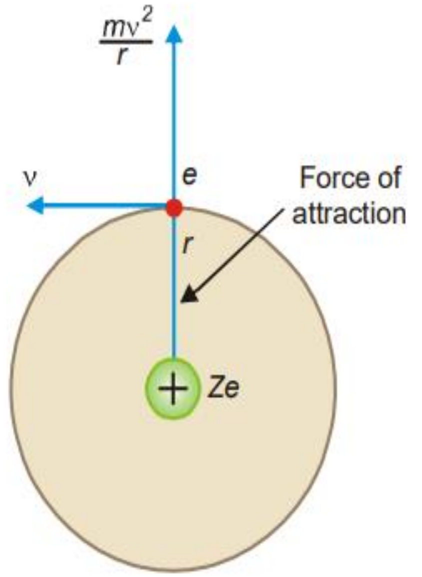


Figure 1.27
Forces keeping electron in orbit.

Energy of electron in each orbit

$$E = \frac{1}{2}\frac{e^2}{r} - \frac{e^2}{r}$$

or $$E = -\frac{e^2}{2r}$$

Substituting the value of r from equation (4) in (8)

$$E = -\frac{e^2}{2} \times \frac{4\pi^2 me^2}{n^2 h^2}$$

$$= -\frac{2\pi^2 me^4}{n^2 h^2}$$

Substituting the values of m, e, and h in (9),

$$E = \frac{-2.179 \times 10^{-11}}{n^2} \text{ erg/atom}$$

or $$E = \frac{-2.179 \times 10^{-18}}{n^2} \text{ J per atom}$$

or $$E = \frac{-2.17 \times 10^{18} \times 6.02 \times 10^{23}}{n^2} \text{ J per mole}$$

or $$E = \frac{-1311.8}{n^2} \text{ kJ per mole}$$

or $$E = \frac{-313.3}{n^2} \text{ kcal per mole}$$

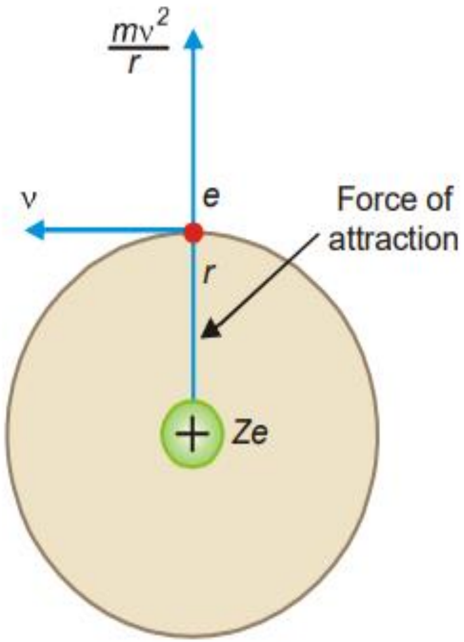


Figure 1.27
Forces keeping electron in orbit.

Mathematical Problem

- Calculate the first five Bohr radii.

- Calculate the five lowest energy levels of the hydrogen atom

Limitations of Bohr Theory

- Bohr theory successfully explain spectrum of hydrogen, but can not explain the spectral lines of atoms with more than one electron.

- This theory is unrealistic in the sense that periodic motion around a central body usually follows an elliptical path rather than a circular path which has been assumed in the case of Bohr theory. If electrons follow elliptical path, the velocity along the path does not remain constant.

- According to Bohr's model when an electron jumps from one energy level to another, a single line is supposed to appear on the spectra. However, when a spectrograph is developed with high resolving power there are two or more lines very close together are observed. Bohr's atom model gives no explanation on this.

Limitations of Bohr Theory

- When spectra were examined with spectrometers, each line was found to consist of several closely packed lines

Zeeman Effect:

- In 1896 Zeeman discovered that spectral lines are split up into components when the source emitting lines is placed in a strong magnetic field.

- It is called the Zeeman effect after the name of the discoverer

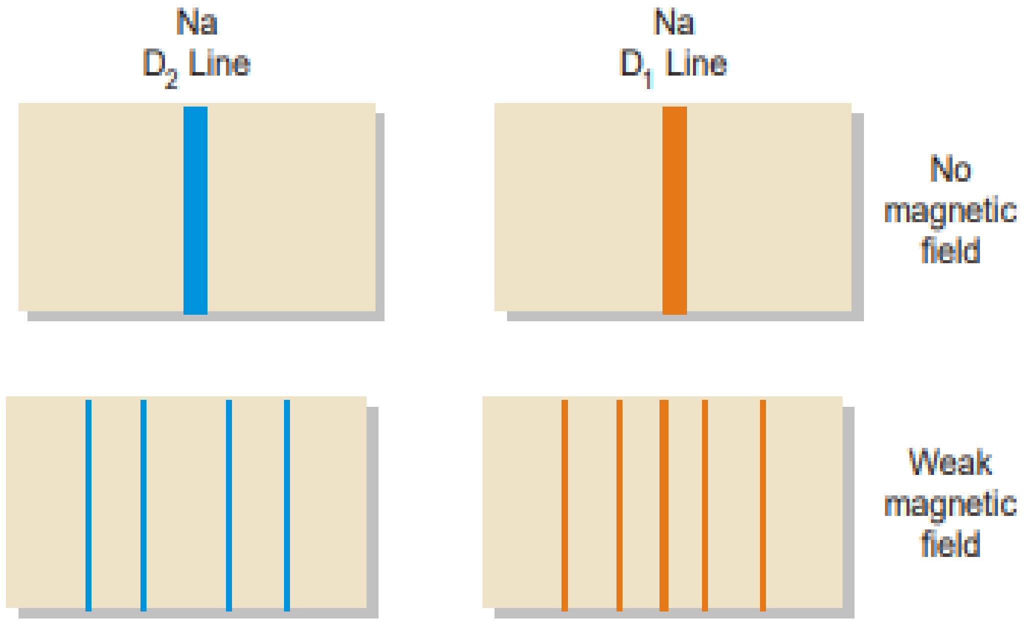


Figure 1.33
Splitting of the D_2 and D_1 lines in the sodium spectrum by a weak magnetic field (Illustration of Zeeman effect).

Wave Mechanical Concept of Atom

Classical 'mechanical theory' of matter:

- considered matter to be made of discrete particles (atoms, electrons, protons etc.), called the '

Wave theory :

- another theory that was necessary to interpret the nature of radiations like X-rays and light.
- According to the wave theory, radiations as X-rays and light, consisted of continuous collection of waves travelling in space.

Wave Mechanical Concept of Atom

Quantum Concept and "Wave Mechanical Theory":

- Planck and Einstein (1905) proposed that energy radiations, including those of heat and light, are emitted discontinuously as little 'bursts', quanta, or photons.

- This view is directly opposed to the wave theory of light and it gives particle-like properties to waves.

- According to it, light exhibits both a wave and a particle nature, under suitable conditions.

- This theory which applies to all radiations, is often referred to as the 'Wave Mechanical Theory'

Wave mechanical theory

Wave mechanical theory of atom/matter:

- In 1924 Louis de Broglie advanced a complimentary hypothesis for material particles.
- According to it, the dual character–the wave and particle–may not be confined to radiations alone but should be extended to matter as well.
- In other words, matter also possessed particle as well as wave character.
- This gave birth to the 'Wave mechanical theory of matter'.

De Broglie's Equation

- The momentum of a particle in motion is inversely proportional to wavelength
- Planck's constant 'h' being the constant of this proportionality.
- The wavelength of waves associated with a moving material particle (matter waves) is called de Broglie's wavelength.

de Broglie had arrived at his hypothesis with the help of Planck's Quantum Theory and Einstein's Theory of Relativity. He derived a relationship between the magnitude of the wavelength associated with the mass 'm' of a moving body and its velocity. According to Planck, the photon energy 'E' is given by the equation

$$E = h\nu \qquad \text{...}(i)$$

where h is Planck's constant and ν the frequency of radiation. By applying Einstein's mass-energy relationship, the energy associated with photon of mass 'm' is given as

$$E = mc^2 \qquad \text{...}(ii)$$

where c is the velocity of radiation

Comparing equations (i) and (ii)

$$mc^2 = h\nu = h\frac{c}{\lambda} \qquad \left(\because \nu = \frac{c}{\lambda}\right)$$

or
$$mc = \frac{h}{\lambda} \qquad \text{...}(iii)$$

or
$$\text{mass} \times \text{velocity} = \frac{h}{\text{wavelength}}$$

or
$$\text{momentum } (p) = \frac{h}{\text{wavelength}}$$

or
$$\text{momentum} \propto \frac{1}{\text{wavelength}}$$

De Broglie's Equation

- The de Broglie's equation is true for all particles, but
- it is only with very small particles, such as electrons, that the wave-like aspect is of any significance.
- Large particles in motion though possess wavelength, but it is not measurable or observable

De Broglie's Equation

- Let us, for instance consider de Broglie's wavelengths associated with two bodies and compare their values.

For a large mass:

- Let us consider a stone of mass 100 g moving with a velocity of 1000 cm/sec. The de Broglie's wavelength λ will be given as follows:

$$\lambda = \frac{6.6256 \times 10^{-27}}{100 \times 1000} \qquad \left(\lambda = \frac{h}{\text{momentum}}\right)$$

$$= 6.6256 \times 10^{-32} \text{cm}$$

- This is too small to be measurable by any instrument and hence no significance.

De Broglie's Equation

For a small mass:

- Let us now consider an electron in a hydrogen atom.
- It has a mass= 9.1091×10^{-28} g and
- Moves with a velocity 2.188×10^{-8} cm/sec.
- The de Broglie's wavelength λ is given as

$$\lambda = \frac{6.6256 \times 10^{-27}}{9.1091 \times 10^{-28} \times 2.188 \times 10^{-8}}$$
$$= 3.32 \times 10^{-8}\ \text{cm}$$

- This value is quite comparable to the wavelength of X-rays and hence detectable.

The Wave Nature Of Electron

- de Broglie's revolutionary suggestion was that moving electrons had waves of definite wavelength associated with them

- This idea was put to the acid test by Davison and Germer (1927).

- They demonstrated the physical reality of the wave nature of electrons by showing that a beam of electrons could also be diffracted by crystals just like light or X-rays.

- They observed that the diffraction patterns thus obtained were just similar to those in case of X-rays

The Wave Nature Of Electron

- Since diffraction is a property exclusively of wave motion, Davison and Germer's 'electron diffraction' experiment established beyond doubt the wave nature of electrons

- Therefore, that electrons not only behave like 'particles' in motion but also have 'wave properties' associated with them.

- The application of de Broglie's equation to Bohr's theory produces an important result. (next slide)

The Wave Nature Of Electron

- The quantum restriction of Bohr's theory for an electron in motion in the circular orbit is that the angular momentum (mvr) is an integral multiple (n) of h/2π

$$mvr = n\frac{h}{2\pi}$$

- On rearranging, we get……….

$$2\pi r = n\frac{h}{mv}$$

from equation (i), we ha

$$2\pi r = n\lambda$$

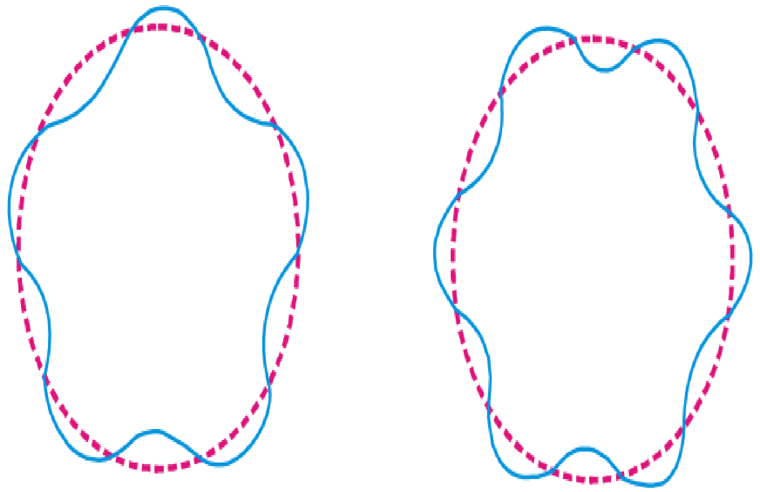


Figure 2.2
de Broglie's wave accommodated in Bohr's orbits. For these two wave trains the value of n is different.

"electron wave of wavelength λ can be accommodated in Bohr's orbit only if the circumference of the orbit, 2πr, is an integral multiple of its wavelength"

Thank you