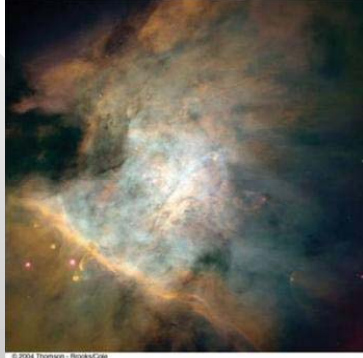# Atomic Models

- Much of the luminous matter in the Universe is hydrogen. In fact hydrogen is the most abundance atom in the Universe. The colours of this Orion Nebula come from the transition between the quantized states in hydrogen atoms.

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INTRODUCTION

- The purpose of this chapter is to build a simplest atomic model that will help us to understand the structure of atoms
- This is attained by referring to some basic experimental facts that have been gathered since 1900's (e.g. Rutherford scattering experiment, atomic spectral lines etc.)
- In order to build a model that well describes the atoms which are consistent with the experimental facts, we need to take into account the wave nature of electron
- This is one of the purpose we explore the wave nature of particles in previous chapters

Basic properties of atoms

- 1)   Atoms are of microscopic size, ~ 10^{-10} m. Visible light is not enough to resolve (see) the detail structure of an atom as its size is only of the order of 100 nm.
- 2)   Atoms are stable
- 3)   Atoms contain negatively charges, electrons, but are electrically neutral. An atom with Z electrons must also contain a net positive charge of $+Ze$.
- 4)   Atoms emit and absorb EM radiation (in other words, atoms interact with light quite readily)

   Because atoms interacts with EM radiation quite strongly, it is usually used to probe the structure of an atom. The typical of such EM probe can be found in the atomic spectrum as we will see now

Emission spectral lines

- Experimental fact: A single atom or molecule in a very diluted sample of gas emits radiation characteristic of the particular atom/molecule species
- The emission is due to the de-excitation of the atoms from their excited states
- e.g. if heating or passing electric current through the gas sample, the atoms get excited into higher energy states
- When a excited electron in the atom falls back to the lower energy states (de-excites), EM wave is emitted

- The spectral lines are analysed with *spectrometer*, which give important physical information of the atom/molecules by analysing the wavelengths composition and pattern of these lines.
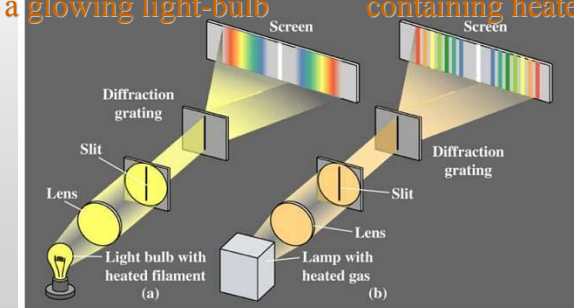
Line spectrum of an atom

- The light given off by individual atoms, as in a low-pressure gas, consist of a series of discrete wavelengths corresponding to different colour.
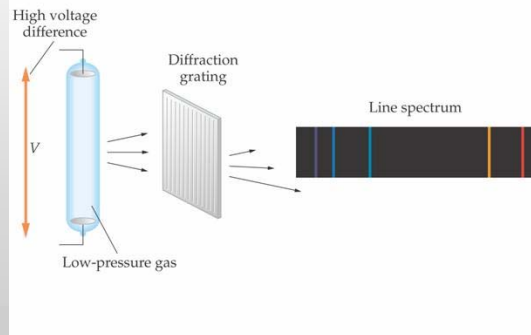
5

Comparing continuous and line spectrum

- (a) continuous spectrum produced by a glowing light-bulb
- (b) Emission line spectrum by lamp containing heated gas

6

Absorption line spectrum

- We also have absorption spectral line, in which white light is passed through a gas. The absorption line spectrum consists of a bright background crossed by dark lines that correspond to the absorbed wavelengths by the gas atom/molecules.

7

Experimental arrangement for the observation of the absorptions lines of a sodium vapour
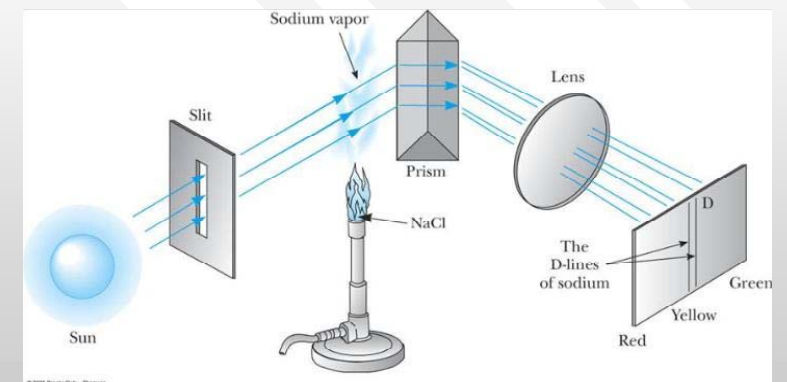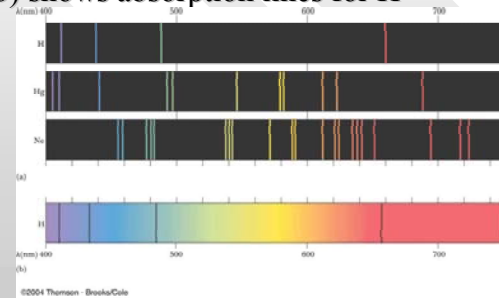
Comparing emission and absorption spectrum

The emitted and absorption radiation displays characteristic discrete sets of spectrum which contains certain discrete wavelengths only

(a) shows 'finger print' emission spectral lines of H, Hg and Ne. (b) shows absorption lines for H

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9

A successful atomic model must be able to explain the observed discrete atomic spectrum

We are going to study two attempts to built model that describes the atoms: the Thompson Plum-pudding model (which fails) and the Rutherford-Bohr model (which succeeds)

10

The Thompson model – Plum-pudding model

Sir J. J. Thompson (1856-1940) is the Cavandish professor in Cambridge who discovered electron in cathode rays. He was awarded Nobel prize in 1906 for his research on the conduction of electricity by bases at low pressure.
He is the first person to establish the particle nature of electron. Ironically his son, another renown physicist proves experimentally electron behaves like wave…
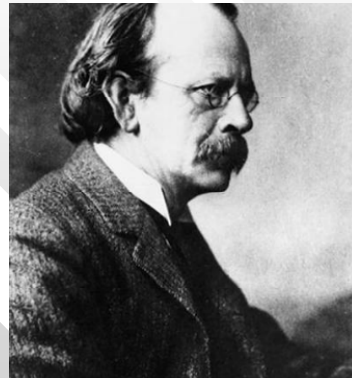
11

Plum-pudding model

- An atom consists of Z electrons is embedded in a cloud of positive charges that exactly neutralise that of the electrons'
- The positive cloud is heavy and comprising most of the atom's mass
- Inside a stable atom, the electrons sit at their respective equilibrium position where the attraction of the positive cloud on the electrons balances the electron's mutual repulsion

12

Slide 13

Thompson plum pudding
model of the atom

Negative electron plums

Positive pudding

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One can treat the electron in the pudding like a point mass stressed by two springs

SHM

The "electron plum" stuck on the pudding vibrates and executes SHM

- The electron at the EQ position shall vibrate like a simple harmonic oscillator with a frequency

$$\nu = \left(\frac{1}{2\pi}\right)\sqrt{\frac{k}{m}}$$

- Where $k = \dfrac{Ze^2}{4\pi\varepsilon_o R^3}$, R radius of the atom, m mass of the electron

- From classical EM theory, we know that an oscillating charge will emit radiation with frequency identical to the oscillation frequency ν as given above

The plum-pudding model predicts unique oscillation frequency

- Radiation with frequency identical to the oscillation frequency.
- Hence light emitted from the atom in the plum-pudding model is predicted to have exactly one unique frequency as given in the previous slide.
- This prediction has been falsified because observationally, light spectra from all atoms (such as the simplest atom, hydrogen,) have sets of discrete spectral lines correspond to many different frequencies (already discussed earlier).

Experimental verdict on the plum pudding model

- Theoretically one expect the deviation angle of a scattered particle by the plum-pudding atom to be small: $\Theta = \sqrt{N}\theta_{ave} \sim 1°$
- This is a prediction of the model that can be checked experimentally
- Rutherford was the first one to carry out such experiment

FIGURE 6.2 A positively charged alpha particle is deflected by an angle θ as it passes through a Thomson-model atom. The coordinates r and ϕ locate the alpha particle while it is inside the atom.

FIGURE 6.6 A microscopic representation of the scattering. Some individual scatterings tend to increase Θ, while others tend to decrease Θ.

Ernest Rutherford

British physicist Ernest Rutherford, winner of the 1908 Nobel Prize in chemistry, pioneered the field of nuclear physics with his research and development of the nuclear theory of atomic structure

Born in New Zealand, teachers to many physicists who later become Nobel prize laureates

Rutherford stated that an atom consists largely of empty space, with an electrically positive nucleus in the center and electrically negative electrons orbiting the nucleus. By bombarding nitrogen gas with *alpha particles* (nuclear particles emitted through radioactivity), Rutherford engineered the transformation of an atom of nitrogen into both an atom of oxygen and an atom of hydrogen.

This experiment was an early stimulus to the development of nuclear energy, a form of energy in which nuclear transformation and disintegration release extraordinary power.

Rutherford experimental setup

- Alpha particles from source is used to be scattered by atoms from the thin foil made of gold
- The scattered alpha particles are detected by the background screen

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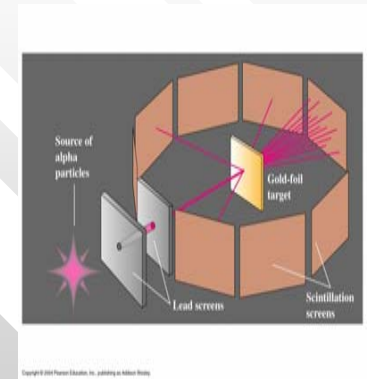
"…fire a 15 inch artillery shell at a tissue paper and it came back and hit you"

- In the scattering experiment Rutherford saw some electrons being bounced back at 180 degree.
- He said this is like firing "a 15-inch shell at a piece of a tissue paper and it came back and hit you"
- Hence Thompson plum-pudding model fails in the light of these experimental result


So, is the plum pudding model utterly useless?

- So the plum pudding model does not work as its predictions fail to fit the experimental data as well as other observations
- Nevertheless it's a perfectly sensible scientific theory because:
- It is a mathematical model built on sound and rigorous physical arguments
- It predicts some physical phenomenon with definiteness
- It can be verified or falsified with experiments
- It also serves as a prototype to the next model which is built on the experience gained from the failure of this model

How to interpret the Rutherford scattering experiment?

- The large deflection of alpha particle as seen in the scattering experiment with a thin gold foil must be produced by a close encounter between the alpha particle and a very small but massive kernel inside the atom

- In contrast, a diffused distribution of the positive charge as assumed in plum-pudding model cannot do the job

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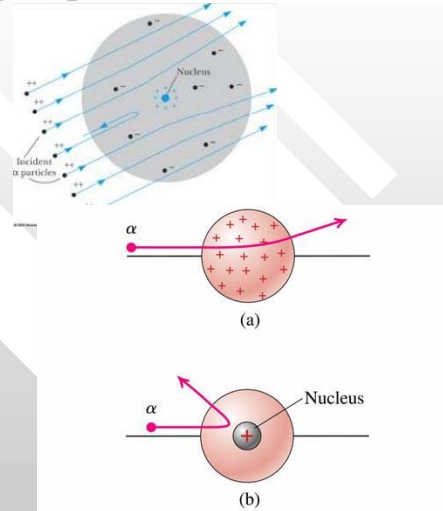
Comparing model with nucleus concentrated at a point-like nucleus and model with nucleus that has large size
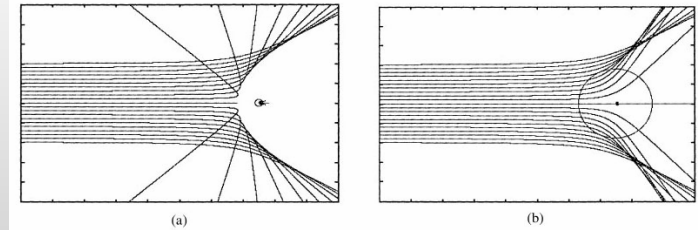

Recap
the atomic model building story

- Plum-pudding model by Thompson
- It fails to explain the emission and absorption line spectrum from atoms because it predicts only a single emission frequency

$$v = \left(\frac{1}{2\pi}\right)\sqrt{\frac{k}{m}}$$

- Most importantly it fails to explain the back-scattering of alpha particle seen in Rutherford's scattering experiment because the model predicts only $\Theta = \sqrt{N}\theta_{ave} \sim 1°$
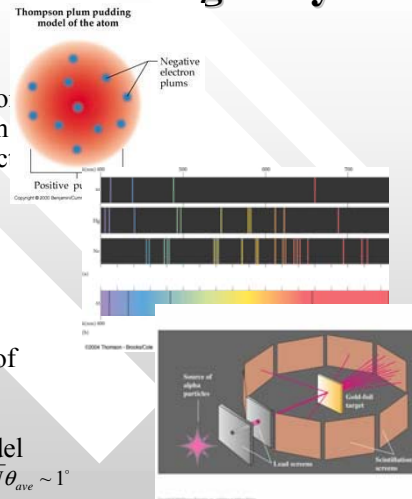
The Rutherford model
(planetary model)

- Rutherford put forward an model to explain the result of the scattering experiment: the Rutherford model

- An atom consists of a very small nucleus of charge $+Ze$ containing almost all of the mass of the atom; this nucleus is surrounded by a swarm of Z electrons
- The atom is largely comprised of empty space
- $R_{atom} \sim 10^{-10}$m
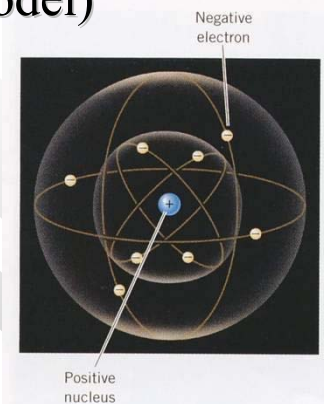- $R_{nucleus} \sim 10^{-13}$ - 10^{-15} m

Figure 30.1 In the nuclear atom a small positively charged nucleus is surrounded at relatively large distances by a number of electrons.

Infrared catastrophe: insufficiency of the Rutherford model

- According to classical EM, the Rutherford model for atom (a classical model) has a fatal flaw: it predicts the collapse of the atom within 10^{-10} s
- A accelerated electron will radiate EM radiation, hence causing the orbiting electron to loss energy and consequently spiral inward and impact on the nucleus
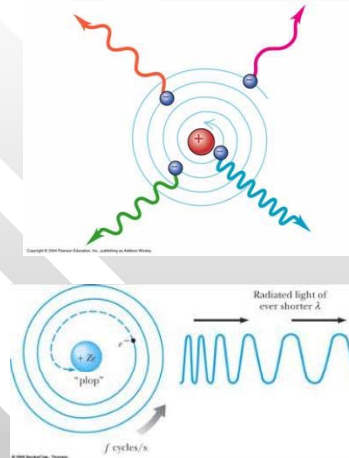
Rutherford model also can't explain the discrete spectrum

- The Rutherford model also cannot explain the pattern of discrete spectral lines as the radiation predicted by Rutherford model is a continuous burst.

So how to fix up the problem?

NEILS BOHR COMES TO THE RESCUE

- **Niels Bohr** (1885 to 1962) is best known for the investigations of atomic structure and also for work on radiation, which won him the 1922 Nobel Prize for physics
- He was sometimes dubbed "the God Father" in the physicist community
- http://www-gap.dcs.st-and.ac.uk/~history/Mathematicians/Bohr_Niels.html

To fix up the infrared catastrophe …

Neils Bohr put forward a model which is a hybrid of the Rutherford model with the wave nature of electron taken into account

Bohr's model of hydrogen-like atom

- We shall consider a simple atom consists of a nucleus with charge Ze and mass of $M_{nucleus} << m_e$
- The nucleus is urrounded by only a single electron
- We will assume the centre of the circular motion of the electron coincides with the centre of the nucleus
- We term such type of simple system: hydrogen-like atoms
- For example, hydrogen atom corresponds to $Z = 1$; a singly ionised Helium atom He^+ corresponds to $Z = 2$ etc
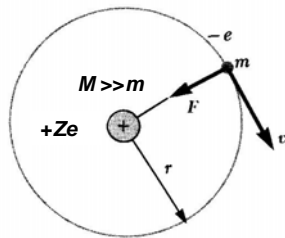

$M >> m$

$+Ze$

$-e$
m
F
v
r

Diagram representing the model of a hydrogen-like atom

29

Bohr's postulate, 1913

- Postulate No.1: Mechanical stability (classical mechanics)
- An electron in an atom moves in a circular orbit about the nucleus under Coulomb attraction obeying the law of classical mechanics
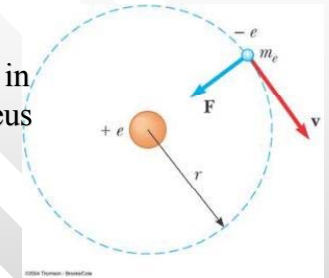
Coulomb's attraction = centripetal force

$$\frac{1}{4\pi\varepsilon_0}\frac{(Ze)e}{r^2} = \frac{m_e v^2}{r}$$

Assumption: the mass of the nucleus is infinitely heavy compared to the electron's

30

Postulate 2: condition for orbit stability

- Instead of the infinite orbit which could be possible in classical mechanics (c.f the orbits of satellites), it is only possible for an electron to move in an orbit that contains an integral number of de Broglie wavelengths,

- $n\lambda_n = 2\pi r_n$, $n = 1,2,3...$

31

Bohr's 2nd postulate means that n de Broglie wavelengths must fit into the circumference of an orbit

— Electron path
— De Broglie electron wave

Figure 4.12 The orbit of the electron in a hydrogen atom corresponds to a complete electron de Broglie wave joined on itself.

Destructive interference

(a)

(b)
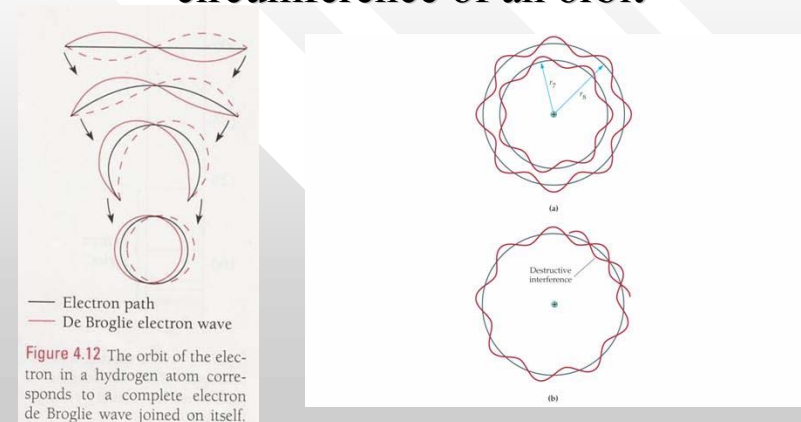
Electron that don't form standing wave

- Since the electron must form standing waves in the orbits, the the orbits of the electron for each n is quantised
- Orbits with the perimeter that do not conform to the quantisation condition cannot persist
- All this simply means: all orbits of the electron in the atom must be quantised, and orbit that is not quantised is not allowed (hence can't exist)

Figure 4.14 A fractional number of wavelengths cannot persist because destructive interference will occur.

Quantisation of angular momentum

- As a result of the orbit quantisation, the angular momentum of the orbiting electron is also quantised:
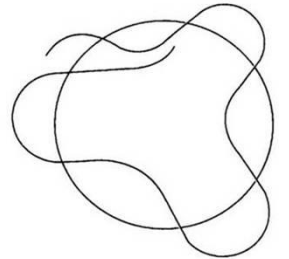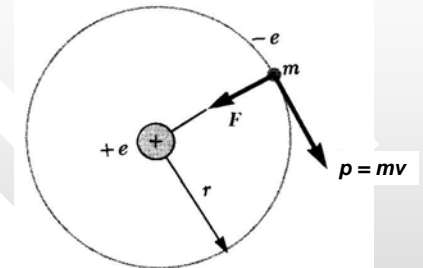- $L = (m_e v)\, r = pr$ (definition)
- $n\lambda = 2\pi r$ (orbit quantisation)
- Combining both:
- $p = h/\lambda = nh/2\pi r$
- $L = m_e vr = p\, r = nh/2\pi$

$p = mv$

Angular momentum of the electron,

$L = p \times r$. It is a vector quantity with its direction pointing to the direction perpendicular to the plane defined by p and r

Third postulate

- Despite the fact that it is constantly accelerating, an electron moving in such an allowed orbit does not radiate EM energy (hence total energy remains constant)
- As far as the stability of atoms is concerned, classical physics is invalid here
- My Comment: At the quantum scale (inside the atoms) some of the classical EM predictions fail (e.g. an accelerating charge radiates EM wave)

Quantisation of velocity and radius

- Combining the quantisation of angular momentum and the equation of mechanical stability we arrive at the result that:
- the allowed radius and velocity at a given orbit are also quantised:

$$r_n = 4\pi\varepsilon_0 \frac{n^2\hbar^2}{m_e Z e^2} \qquad v_n = \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{n\hbar}$$

Some mathematical steps leading to quantisation of orbits,

$$r_n = 4\pi\varepsilon_0 \frac{n^2\hbar^2}{m_e Ze^2}$$

$$m_e vr = \frac{nh}{2\pi} \qquad \text{(Eq.1)}$$

$$\frac{1}{4\pi\varepsilon_0}\frac{(Ze)e}{r^2} = \frac{m_e v^2}{r} \Rightarrow v^2 = \frac{Ze^2}{4\pi\varepsilon_0 m_e}\frac{1}{r} \qquad \text{(Eq. 2)}$$

- (Eq.2) → (Eq.1)^2,
- $(m_e vr)^2 = (nh/2\pi)^2$
- LHS: $m_e^2 r^2 v^2 = m_e^2 r^2 (Ze^2 / 4\pi\varepsilon_0 m_e r)$
  $= m_e r Ze^2 / 4\pi\varepsilon_0 = $ RHS $= (nh/2\pi)^2$
  $r = n^2(h/2\pi)^2 4\pi\varepsilon_0 / Ze^2 m_e \equiv r_n$,
  $n = 1,2,3\ldots$

37

Prove it yourself the quantisation of the electron velocity

$$v_n = \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{n\hbar}$$

using Eq.(1) and Eq.(2)

38

Important comments

- The smallest orbit charaterised by
- $Z = 1$, $n=1$ is the ground state orbit of the hydrogen

$$r_0 = \frac{4\pi\varepsilon_0 \hbar^2}{m_e e^2} = 0.5 \, \overset{0}{A}$$

- It's called the Bohr's radius = the typical size of an atom
- In general, the radius of an hydrogen-like ion/atom with charge Ze in the nucleus is expressed in terms of the Bohr's radius as

$$r_n = n^2 \frac{r_0}{Z}$$

- Note also that the ground state velocity of the electron in the hydrogen atom is $v_0 = 2.2\times10^6$ m/s $\ll c$
- non-relativistic

39

PYQ 7 Test II 2003/04

- In Bohr's model for hydrogen-like atoms, an electron (mass m) revolves in a circle around a nucleus with positive charges Ze. How is the electron's velocity related to the radius r of its orbit?

- **A.** $v = \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{mr}$ **B.** $v = \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{mr^2}$ **C.** $v = \frac{1}{4\pi\varepsilon_0}\frac{Ze}{mr^2}$

- **D.** $v^2 = \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{mr}$ **E.** Non of the above

- Solution: I expect your to be able to derive it from scratch without memorisation
- ANS: D, Schaum's series 3000 solved problems, Q39.13, pg 722 modified

40

The quantised orbits of hydrogen-like atom (not to scale)

$$r_n = n^2 \frac{r_0}{Z}$$

+Ze

r_0

r_4

r_3

r_2
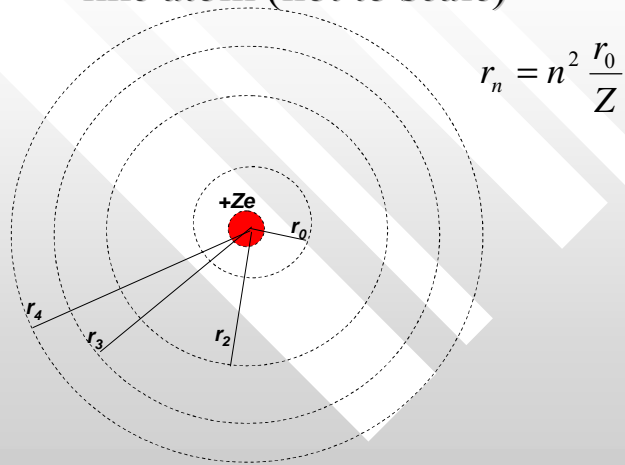
41

Strongly recommending the Physics 2000 interactive physics webpage by the University of Colorado

For example the page
http://www.colorado.edu/physics/2000/quantumzone/bohr.html
provides a very interesting explanation and simulation on atom and Bohr model in particular.
Please visit this page if you go online

42

Recap

- The hydrogen-like atom's radii are quantised according to:

$$r_n = n^2 \frac{r_0}{Z}$$

+Ze
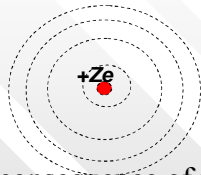
- The quantisation is a direct consequence of the postulate that electron wave forms stationary states (standing waves) at the allowed orbits
- The smallest orbit or hydrogen, the Bohr's radius

$$r_0 = \frac{4\pi\varepsilon_0 \hbar^2}{m_e e^2} = 0.5 \, \overset{0}{A}$$

43

Postulate 4

- Similar to Einstein's postulate of the energy of a photon
  EM radiation is emitted if an electron initially moving in an orbit of total energy E_i, discontinuously changes it motion so that it moves in an orbit of total energy E_f. The frequency of the emitted radiation,

  $\nu = (E_f - E_i)/h$

Figure 30.5 In the Bohr model, a photon is emitted when the electron drops from a larger, higher-energy orbit (energy = E_i) to a smaller, lower-energy orbit (energy = E_f).

Electron

Photon

Nucleus

E_f

E_i

44

Energies in the hydrogen-like atom

- Potential energy of the electron at a distance r from the nucleus is, as we learned from standard electrostatics, ZCT 102, form 6, matriculation etc. is simply
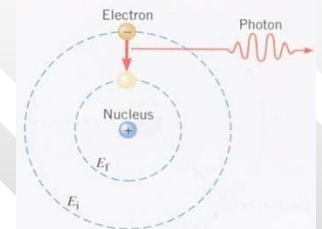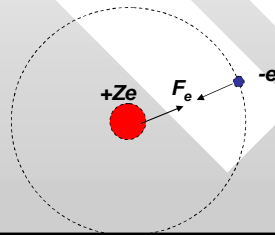
$$V = -\int_r^\infty \frac{Ze^2}{4\pi\varepsilon_0 r^2}\, dr = -\frac{Ze^2}{4\pi\varepsilon_0 r}$$

- -ve means that the EM force is attractive

Kinetic energy in the hydrogen-like atom

- According to definition, the KE of the electron is

$$K = \frac{m_e v^2}{2} = \frac{Ze^2}{8\pi\varepsilon_0 r}$$

The last step follows from the equation $\dfrac{m_e v^2}{r} = \dfrac{Ze^2}{4\pi\varepsilon_0 r^2}$

- Adding up KE + V, we obtain the total mechanical energy of the atom:

$$E = K + V = \frac{Ze^2}{8\pi\varepsilon_0 r} + \left(-\frac{Ze^2}{4\pi\varepsilon_0 r}\right) = -\frac{Ze^2}{8\pi\varepsilon_0}\left(\frac{1}{r}\right) = -\frac{Ze^2}{8\pi\varepsilon_0}\left[\frac{m_e Ze^2}{4\pi\varepsilon_0 n^2 \hbar^2}\right]$$

$$= -\frac{m_e Z^2 e^4}{(4\pi\varepsilon_0)^2 2\hbar^2}\frac{1}{n^2} \equiv E_n$$

The ground state energy

- For the hydrogen atom ($Z = 1$), the ground state energy (which is characterised by $n = 1$)

$$E_0 \equiv E_n(n=1) = -\frac{m_e e^4}{(4\pi\varepsilon_0)^2 2\hbar^2} = -13.6\,\text{eV}$$

In general the energy level of a hydrogen like atom with Ze nucleus charges can be expressed in terms of

$$E_n = \frac{Z^2 E_0}{n^2} = -\frac{13.6 Z^2}{n^2}\,\text{eV}$$

Quantisation of energy levels

- The energy level of the electrons in the atomic orbit is quantised
- The quantum number, n, that characterises the electronic states is called principle quantum number
- Note that the energy state is –ve (because it's a bounded system)

$$E_n = \frac{E_0}{n^2} = -\frac{13.6}{n^2}\,\text{eV}$$
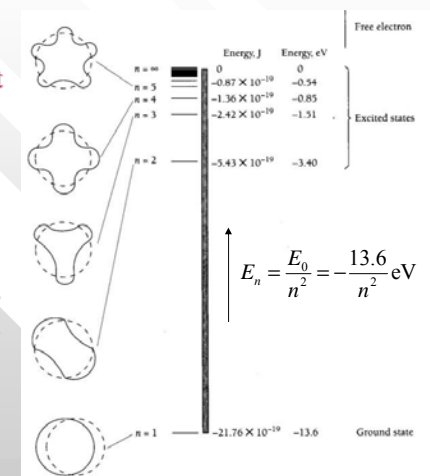
Energy of the electron at very large n

- An electron occupying an orbit with very large n is "almost free" because its energy approaches zero:
$$E_n (n \to \infty) = 0$$
- $E = 0$ means the electron is free from the bondage of the nucleus' potential field
- Electron at high n is not tightly bounded to the nucleus by the EM force
- Energy levels at high n approaches to that of a continuum, as the energy gap between adjacent energy levels become infinitesimal in the large n limit

---

Ionisation energy of the hydrogen atom

- The energy input required to remove the electron from its ground state to infinity (ie. to totally remove the electron from the bound of the nucleus) is simply
$$E_{ionisation} = E_\infty - E_0 = -E_0 = 13.6 \text{eV}$$
- this is the ionisation energy of hydrogen

Ionisation energy to pull the electron off from the attraction of the +ve nucleus

$E=E_0=$-13.6 eV

+Ze F_e -e

+   -e

+Ze

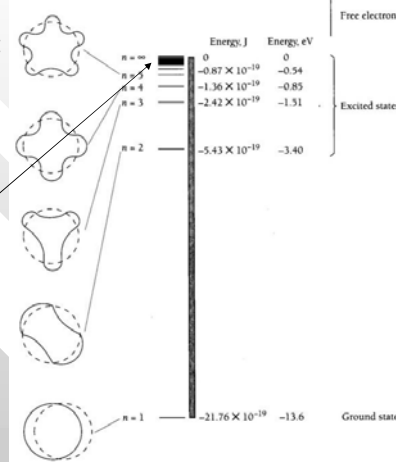*Free electron (= free from the attraction of the +ve nuclear charge, E= 0)*
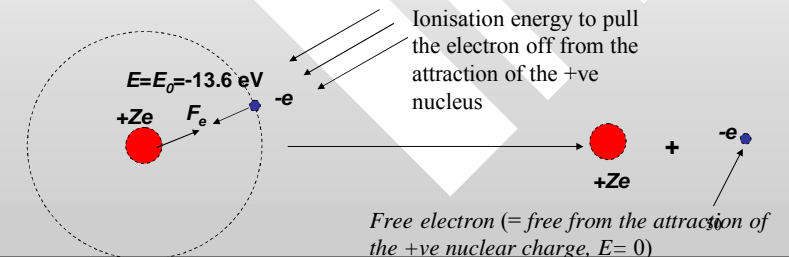
Two important quantities to remember

- As a practical rule, it is strongly advisable to remember the two very important values

- (i) the Bohr radius, $r_0 = 0.53$A and
- (ii) the ground state energy of the hydrogen atom, $E_0 = $ -13.6 eV

Bohr's 4th postulate explains the line spectrum

- When atoms are excited to an energy state above its ground state, they shall radiate out energy (in forms of photon) within at the time scale of $\sim 10^{-8}$ s upon their de-excitations to lower energy states –emission spectrum explained

- When a beam of light with a range of wavelength from sees an atom, the few particular wavelengths that matches the allowed energy gaps of the atom will be absorbed, leaving behind other unabsorbed wavelengthsto become the bright background in the absorption spectrum. Hence absorption spectrum explained

Balmer series and the empirical emission spectrum equation

- Since 1860 – 1898 Balmer have found an empirical formula that correctly predicted the wavelength of four visible lines of hydrogen:

$$\frac{1}{\lambda} = R_H\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$$

$n \to \infty$ $n = 5$ $n = 4$ $n = 3$

$\lambda\,(\text{nm})$ 486.1   656.3 H_α

H_β

H_∞ $n = 6$

364.6   410.2   434.1

H_γ H_δ

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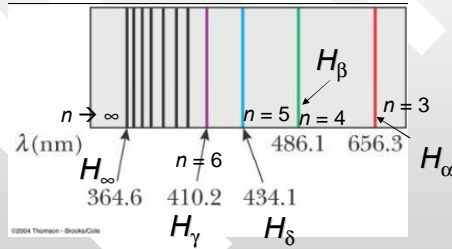
where $n = 3,4,5,\ldots$. R_H is called the Rydberg constant, experimentally measured to be $R_H = 1.0973732 \times 10^7\ \text{m}^{-1}$

53

Example

- For example, for the H_β (486.1 nm) line, $n = 4$ in the empirical formula

$$\frac{1}{\lambda} = R_H\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$$

- According to the empirical formula the wavelength of the hydrogen beta line is

$$\frac{1}{\lambda_\beta} = R_H\left(\frac{1}{2^2} - \frac{1}{4^2}\right) = R_H\left(\frac{3}{16}\right) = \frac{3(1.0973732 \times 10^7\,\text{m}^{-1})}{16}$$

$$\Rightarrow \lambda_\beta = 486\,\text{nm}$$

- which is consistent with the observed value

54

Other spectra series

- Apart from the Balmer series others spectral series are also discovered: Lyman, Paschen and Brackett series

- The wavelengths of these spectral lines are also given by the similar empirical equation as

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

                Lyman series, ultraviolet region

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

                Paschen series, infrared region

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

                Brackett series, infrared region

55

These are experimentally measured spectral line

Lyman series   Balmer series   Paschen series

100   400   1000 λ (nm)

Ultraviolet   Visible light   Infrared

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

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

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

56

Slide 57

Balmer series (visible light)
Paschen series (infrared)
Lyman series (ultraviolet)
Brackett series (infrared)
Pfund series (infrared)

$n = 1$
$n = 2$
$n = 3$
$n = 4$
$n = 5$
$n = 6$
(a)

$n = 7$ -0.28 eV
$n = 6$ -0.38 eV
$n = 5$ -0.54 eV
$n = 4$ -0.85 eV
$n = 3$ -1.51 eV

Lyman series, Paschen series, Pfund series
Brackett series
$n = 2$ -3.40 eV
Balmer series
$n = 1$ -13.6 eV

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

For Lyman series, $n_f = 1$, $n_i = 2, 3, 4, ...$
For Balmer series, $n_f = 2$, $n_i = 3, 4, 5, ...$
For Paschen series, $n_f = 3$, $n_i = 4, 5, 6, ...$

For Brackett series, $n_f = 4$, $n_i = 5, 6, 7, ...$
For Pfund series, $n_f = 5$, $n_i = 6, 7, 8, ...$

57

Slide 58

The empirical formula needs a theoretical explanation

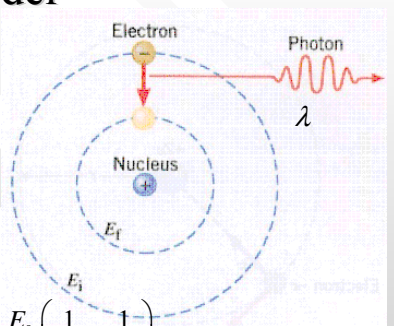$$\frac{1}{\lambda} = R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

is an empirical formula with R_H measured to be $R_H = 1.0973732 \times 10^7$ m^{-1}.

Can the Bohr model provide a sound theoretical explanation to the form of this formula and the numerical value of R_H in terms of known physical constants?

The answer is: YES

58

Slide 59

Theoretical derivation of the empirical formula from Bohr's model

- According to the 4th postulate,
  $\Delta E = E_i - E_f = h\nu = hc/\lambda$, and
- $E_k = E_0 / n_k^2$
- $= -13.6$ eV $/ n_k^2$
- where $k = i$ or j
- Hence we can easily obtain the theoretical expression for the emission line spectrum of hydrogen-like atom

Electron
Photon
λ
Nucleus
E_f
E_i

$$\frac{1}{\lambda} = \frac{\nu}{c} = \frac{E_i - E_f}{ch} = \frac{E_0}{ch} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

$$= \frac{m_e e^4}{4c\pi\hbar^3 (4\pi\varepsilon_0)^2} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \equiv R_\infty \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

59

Slide 60

The theoretical Rydberg constant

$$R_\infty \equiv \frac{m_e e^4}{4c\pi\hbar^3 (4\pi\varepsilon_0)^2} = 1.0984119 \times 10^7 \text{ m}^{-1}$$

- The theoretical Rydberg constant, R_∞, agrees with the experimental one up a precision of less than 1%

$$R_H = 1.0973732 \times 10^7 \text{ m}^{-1}$$

This is a remarkable experimental verification of the correctness of the Bohr model

60

Real life example of atomic emission

- AURORA are caused by streams of fast photons and electrons from the sun that excite atoms in the upper atmosphere. The green hues of an auroral display come from oxygen

Example

- Suppose that, as a result of a collision, the electron in a hydrogen atom is raised to the second excited state ($n = 3$).
- What is (i) the energy and (ii) wavelength of the photon emitted if the electron makes a direct transition to the ground state?
- What are the energies and the wavelengths of the two photons emitted if, instead, the electron makes a transition to the first excited state ($n=2$) and from there a subsequent transition to the ground state?

Make use of $E_k = E_0 / n_k^2 = $ -13.6 eV / n_k^2

The energy of the proton emitted in the transition from the $n = 3$ to the $n = 1$ state is

$$\Delta E = E_3 - E_1 = -13.6\left(\frac{1}{3^2} - \frac{1}{1^2}\right)eV = 12.1eV$$

the wavelength of this photon is
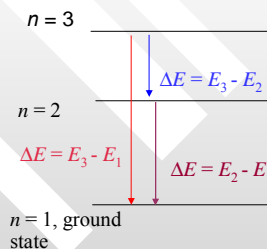
$$\lambda = \frac{c}{v} = \frac{ch}{\Delta E} = \frac{1242 eV \cdot nm}{12.1 eV} = 102nm$$

Likewise the energies of the two photons emitted in the transitions from n = 3 → n = 2 and n = 2 → n = 1 are, respectively,

$$\Delta E = E_3 - E_2 = -13.6\left(\frac{1}{3^2} - \frac{1}{2^2}\right) = 1.89eV \text{ with wavelength}$$

$$\lambda = \frac{ch}{\Delta E} = \frac{1242 eV \cdot nm}{1.89 eV} = 657nm$$

$$\Delta E = E_2 - E_1 = -13.6\left(\frac{1}{2^2} - \frac{1}{1^2}\right) = 10.2eV \text{ with wavelength}$$

$$\lambda = \frac{ch}{\Delta E} = \frac{1242 eV \cdot nm}{10.2 eV} = 121nm$$

$n = 3$

$\Delta E = E_3 \text{ - } E_2$

$n = 2$

$\Delta E = E_3 \text{ - } E_1$

$\Delta E = E_2 \text{ - } E_1$

$n = 1$, ground state

Example

- The series limit of the Paschen ($n_f = 3$) is 820.1 nm (The series limit of a spectral series is the wavelength corresponds to $n_i \to \infty$).
- What are two longest wavelengths of the Paschen series?

Paschen series

800   1000   1200   1400   1600   1800   2000
Wavelength (nm)
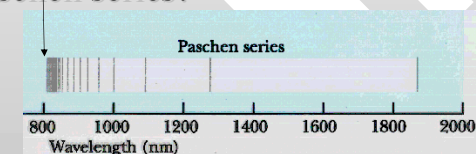
Solution

- Note that the Rydberg constant is not provided
- But by definition the series limit and the Rydberg constant is closely related
- We got to make use of the series limit to solve that problem
- By referring to the definition of the series limit,

$$\frac{1}{\lambda} = R_H\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \xrightarrow{n_i \to \infty} \frac{1}{\lambda_\infty} = \frac{R_H}{n_f^2}$$

- Hence we can substitute $R_H = n_f^2 / \lambda_\infty$ into

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

- and express it in terms of the series limit as

$$\frac{1}{\lambda} = \frac{1}{\lambda_\infty}\left(1 - \frac{n_f^2}{n_i^2}\right)$$

- n = 4,5,6…

65

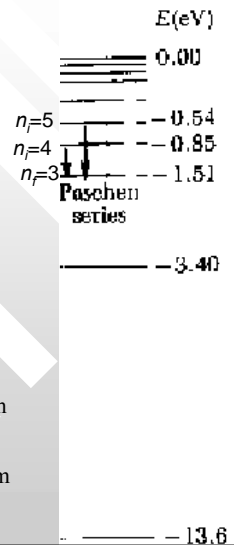- For Paschen series, $n_f = 3, \lambda_\infty = 820.1$ nm

$$\frac{1}{\lambda} = \frac{1}{820.1\,\text{nm}}\left(1 - \frac{3^2}{n_i^2}\right)$$

- The two longest wavelengths correspond to transitions of the two smallest energy gaps from the energy levels closest to $n = 3$ state (i.e the $n = 4$, $n = 5$ states) to the $n = 3$ state

$$n_i = 4: \lambda = 820.1\,\text{nm}\left(\frac{n_i^2}{n_i^2 - 9}\right) = 820.1\,\text{nm}\left(\frac{4^2}{4^2 - 9}\right) = 1875\,\text{nm}$$

$$n_i = 5: \lambda = 820.1\,\text{nm}\left(\frac{n_i^2}{n_i^2 - 9}\right) = 820.1\,\text{nm}\left(\frac{5^2}{5^2 - 9}\right) = 1281\,\text{nm}$$

E(eV)
0.00
$n_i=5$ −0.54
$n_i=4$ −0.85
$n_f=3$ −1.51
Paschen series
−3.40
−13.6

Example

- Given the ground state energy of hydrogen atom -13.6 eV, what is the longest wavelength in the hydrogen's Balmer series?
- Solution:

$$\Delta E = E_i - E_f = -13.6 \text{ eV } (1/n_i^2 - 1/n_f^2) = hc/\lambda$$

- Balmer series: $n_f = 2$. Hence, in terms of 13.6 eV the wavelengths in Balmer series is given by

$$\lambda_{Balmer} = \frac{hc}{13.6\text{eV}\left(\frac{1}{4} - \frac{1}{n_i^2}\right)} = \frac{1240\text{eV}\cdot\text{nm}}{13.6\text{eV}\left(\frac{1}{4} - \frac{1}{n_i^2}\right)} = \frac{91\text{nm}}{\left(\frac{1}{4} - \frac{1}{n_i^2}\right)}, \quad n_i = 3,4,5...$$

67

$$\lambda_{Balmer} = \frac{91\text{nm}}{\left(\frac{1}{4} - \frac{1}{n_i^2}\right)}, \quad n_i = 3,4,5...$$

- longest wavelength corresponds to the transition from the $n_i = 3$ states to the $n_f = 2$ states
- Hence

$$\lambda_{Balmer,\max} = \frac{91\text{nm}}{\left(\frac{1}{4} - \frac{1}{3^2}\right)} = 655.2\text{nm}$$

- This is the red H_α line in the hydrogen's Balmer series

- Can you calculate the shortest wavelength (the series limit) for the Balmer series? Ans = 364 nm

68

PYQ 2.18 Final Exam 2003/04

- Which of the following statements are true?
- **I.**.   the ground states are states with lowest energy
- **II.**   ionisation energy is the energy required to raise an electron from ground state to free state
- **III**. Balmer series is the lines in the spectrum of atomic hydrogen that corresponds to the transitions to the $n = 1$ state from higher energy states

- **A.** I,IV   **B.** I,II, IV   **C.** I, III,IV
- **D.** I, II   **E.** II,III

- **ANS: D, My own question**
- **(note: this is an obvious typo error with the statement IV missing. In any case, only statement I, II are true.)**

PYQ 1.5 KSCP 2003/04

- An electron collides with a hydrogen atom in its ground state and excites it to a state of n =3. How much energy was given to the hydrogen atom in this collision?
- **A.** -12.1 eV **B.** 12.1 eV **C.** -13.6 eV
- **D.** 13.6 eV   **E.** Non of the above
- **Solution:**
$$\Delta E = E_3 - E_0 = \frac{E_0}{3^2} - E_0 = \frac{(-13.6\text{eV})}{3^2} - (-13.6\text{eV}) = 12.1\text{eV}$$
- **ANS: B**, Modern Technical Physics, Beiser, Example 25.6, pg. 786

Frank-Hertz experiment

- The famous experiment that shows the excitation of atoms to discrete energy levels and is consistent with the results suggested by line spectra
- Mercury vapour is bombarded with electron accelerated under the potential V (between the grid and the filament)
- A small potential V_0 between the grid and collecting plate prevents electrons having energies less than a certain minimum from contributing to the current measured by ammeter
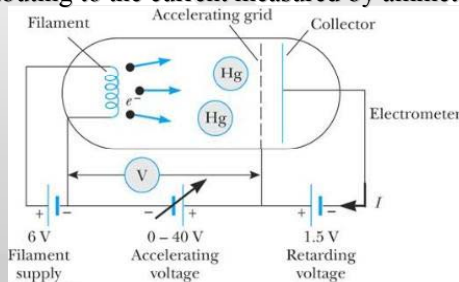
The electrons that arrive at the anode peaks at equal voltage intervals of 4.9 V

- As V increases, the current measured also increases
- The measured current drops at multiples of a critical potential
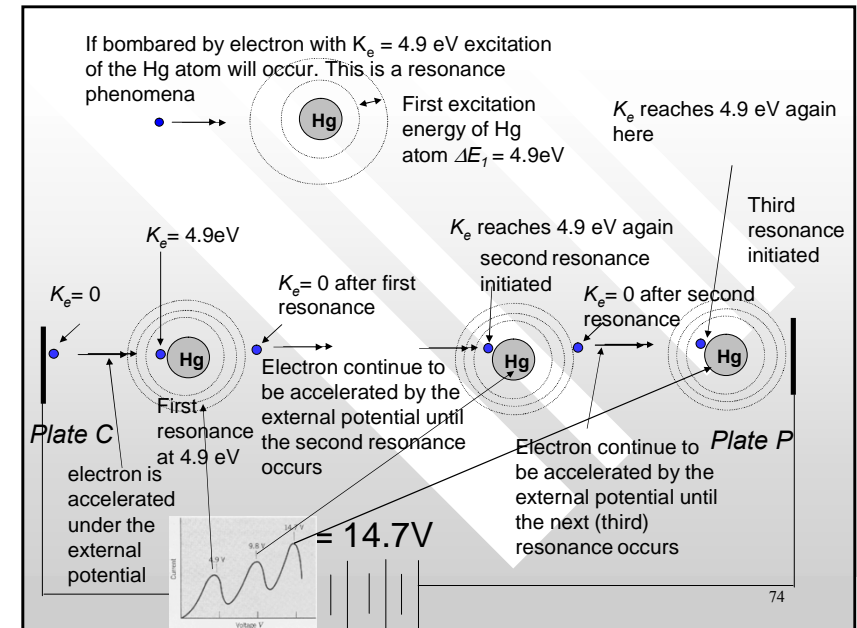- $V = 4.9$ V, 9.8V, 14.7V
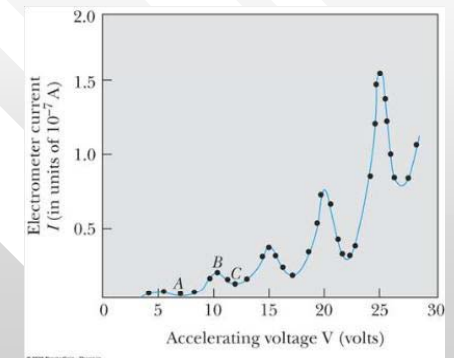
Interpretation

- As a result of inelastic collisions between the accelerated electrons of KE 4.9 eV with the the Hg atom, the Hg atoms are excited to an energy level above its ground state
- At this critical point, the energy of the accelerating electron equals to that of the energy gap between the ground state and the excited state
- This is a resonance phenomena, hence current increases abruptly
- After inelastically exciting the atom, the original (the bombarding) electron move off with too little energy to overcome the small retarding potential and reach the plate
- As the accelerating potential is raised further, the plate current again increases, since the electrons now have enough energy to reach the plate
- Eventually another sharp drop (at 9.8 V) in the current occurs because, again, the electron has collected just the same energy to excite the same energy level in the other atoms

73

If bombared by electron with K_e = 4.9 eV excitation of the Hg atom will occur. This is a resonance phenomena

First excitation energy of Hg atom ΔE_1 = 4.9eV

K_e reaches 4.9 eV again here

Third resonance initiated

K_e = 4.9eV

K_e reaches 4.9 eV again second resonance initiated

K_e = 0 after second resonance

K_e = 0

K_e = 0 after first resonance

Hg

Plate C

First resonance at 4.9 eV

electron is accelerated under the external potential

Electron continue to be accelerated by the external potential until the second resonance occurs

Hg

Electron continue to be accelerated by the external potential until the next (third) resonance occurs

Hg

Plate P

= 14.7V

74

- The higher critical potentials result from two or more inelastic collisions and are multiple of the lowest (4.9 V)
- The excited mercury atom will then de-excite by radiating out a photon of exactly the energy (4.9 eV) which is also detected in the Frank-Hertz experiment
- The critical potential verifies the existence of atomic levels

75

Bohr's correspondence principle

- The predictions of the quantum theory for the behaviour of any physical system must correspond to the prediction of classical physics in the limit in which the quantum number specifying the state of the system becomes very large:

- $\lim_{n \to \infty}$ quantum theory = classical theory

- At large n limit, the Bohr model must reduce to a "classical atom" which obeys classical theory

76

In other words…

- The laws of quantum physics are valid in the atomic domain; while the laws of classical physics is valid in the classical domain; where the two domains overlaps, both sets of laws must give the same result.

PYQ 20 Test II 2003/04

- Which of the following statements are correct?

- **I** Frank-Hertz experiment shows that atoms are excited to discrete energy levels
- **II** Frank-Hertz experimental result is consistent with the results suggested by the line spectra
- **III** The predictions of the quantum theory for the behaviour of any physical system must correspond to the prediction of classical physics in the limit in which the quantum number specifying the state of the system becomes very large
- **IV** The structure of atoms can be probed by using electromagnetic radiation

- **A. II,III**   **B. I, II,IV**   **C. II, III, IV**
- **D. I,II, III, IV**   **E. Non of the above**
- **ANS:D, My own questions**

Example
(Read it yourself)

- Classical EM predicts that an electron in a circular motion will radiate EM wave at the same frequency
- According to the correspondence principle,

  the Bohr model must also reproduce this result in the large n limit

More quantitatively

- In the limit, $n = 10^3 - 10^4$, the Bohr atom would have a size of 10^{-3} m
- This is a large quantum atom which is in classical domain
- The prediction for the photon emitted during transition around the $n = 10^3 - 10^4$ states should equals to that predicted by classical EM theory.

$n \rightarrow$ large
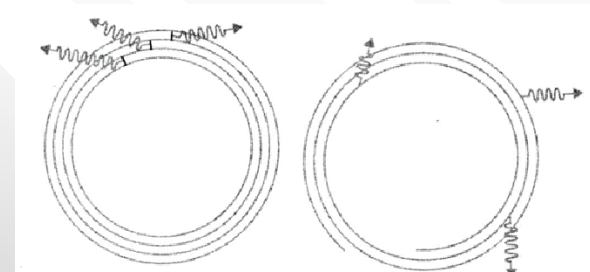
V_n (Bohr) $=$ V (classical theory)

FIGURE 6.26 (Top) A large quantum atom. Photons are emitted in discrete transitions as the electron jumps to lower states. (Bottom) A classical atom. Photons are emitted continuously by the accelerated electron.

Classical physics calculation

- The period of a circulating electron is
$$T = 2\pi r/(2K/m)^{1/2}$$
$$= \pi r(2m)^{1/2}(8\pi e_0 r)^{1/2}/e$$

- This result can be easily derived from the mechanical stability of the atom as per
$$\frac{1}{4\pi\varepsilon_0}\frac{(Ze)e}{r^2} = \frac{m_e v^2}{r}$$

- Substitute the quantised atomic radius $r_n = n^2 r_0$ into T, we obtain the frequency as per
$$\nu_n = 1/T = me^4/32\pi^3\varepsilon_0^2\hbar^3 n^3$$

81

Based on Bohr's theory

- Now, for an electron in the Bohr atom at energy level $n = 10^3 - 10^4$, the frequency of an radiated photon when electron make a transition from the n state to $n-1$ state is given by
$$\nu_n = (me^4/64\pi^3\varepsilon_0^2\hbar^3)[(n-1)^{-2} - n^{-2}]$$
$$= (me^4/64\pi^3\varepsilon_0^2\hbar^3)[(2n-1)/n^2(n-1)^2]$$

In the limit of large n,
$$\nu \approx (me^4/64\pi^3\varepsilon_0^2\hbar^3)[2n/n^4]$$
$$= (me^4/32\pi^3\varepsilon_0^2\hbar^3)[1/n^3]$$

82

Classical result and Quantum calculation meets at $n \rightarrow \infty$

- Hence, in the region of large n, where classical and quantum physics overlap, the classical prediction and that of the quantum one is identical
$$\nu_{classical} = \nu_{Bohr} = (me^4/32\pi^3\varepsilon_0^2\hbar^3)[1/n^3]$$

83