Atomic Structure

Structure of matter always been an interesting area of research for physicists. Till 20th century it was assumed that matter consists of indivisible small tiny particles called "atoms". But with the study and research it was found that the atom is divisible and made of other small particles called electron, proton and Neutron. So may physicists tried to explain the structure of atom but finally it was Neils Bohr whose explanation about the structure was well accepted. For simplicity they have taken hydrogen atom and then it can be extended to other H-like atoms too. Some of the historical models are also explained and them drawbacks:

Thomson's Atomic Model

J.J. thomson found the charge to mass ratio of electron for atomic structure. He describes the atom as a region in which positive charge is spread out in space with electrons embedded throughout the region, much like the seeds in a water - melon. The atom as a whole then be electrically neutral.

Rutherford's Model

In 1911 Earnest, Rutherford and his students performed a critical experiment which showed that Thompson Model may not be correct. They bombarded highly energetic α -Particles be correct. (He^++ Nucleus) onto a thin Gold foil. Following observation were there:

(i) Most of the Practises were passed through the foil as if it were an empty space.
(ii) Very few particles were even deflected backward completely reversing their direction.

(iii) Rest ones were deflected from 0° to 180° to their original direction of motion.
Rutherford concluded that most of the part of atom is empty and all the +ve charge is concentrated at the center in a very small volume he named it nucleus. Electrons are moving around sun. Hence this model was also referred as planetary model of the atom.

There were two basic difficulties with the model reason of characteristic radiation coming from atom. The second was according to maxwell theory of electromagnetic Radiation an orbiting electron i an accelerating charge hence it should emit EM radiations resulting in decrease of radius of orbit and finally it should fall on nucleus. But atom is an stable entity.
Bohr's Model of hydrogen Atom

The first successful picture of atom was given by Bohr. His model was successful in explaining the lines of EM radiations coming out from H₂ gas. Although model is now considered obsolete and has been completely replaced by Quantum - Mechanical Theory but it was historically important to the development of Quantum mechanics.

To explain his model Bohr made some postulates:

(i) Electrons revolve around the nucleus in stationary circular orbits where centripetal acceleration is provided by the coulombic attraction of protons on electrons as:

\[
\left( \frac{1}{4\pi \varepsilon_0} \right) \frac{ze^2}{r^2} = \frac{mv^2}{r}
\]

\( z = \) atomic number

\( m = \) mass of electron

\( r = \) radius of an orbit.

or

\[
\frac{ze^2}{4\pi \varepsilon_0 r} = \frac{mv^2}{r} \quad \text{...(i)}
\]

(ii) Instead of the infinity of orbits which would be possible in classical mechanics, it is only possible for an electron to move in an orbit for which its orbital angular momentum \( L \) is an integral multiple of \( \frac{h}{2\pi} \).

\[
L = mvr = \frac{nh}{2\pi}
\]

\( h = \) Plank's constant

\( n = 1, 2, 3, \ldots \) (Quantized Penissible orbits)

(iii) The electron revolving in any one of these allowed orbits does not radiate. These non-radiating orbits are called stationary orbits.

(iv) Energy of electron changes only when there is a transition from higher orbit to lower or from lower to higher.

\[
E_i \quad \text{and} \quad E_f
\]

Photon of energy \( 'hv' \) is emitted when there is a transition from higher to lower.
Calculating radius \( (r_n) \) and speed \( (v_n) \) of \( n^{th} \) orbit

from eqn (i) and (ii)
we have

\[
r_n = \frac{n^2 h^2 \epsilon_0}{Ze^2 \pi m} = \frac{(0.53 \text{ Å})}{z} n^2
\]

and

\[
v_n = \frac{Ze^2}{2nh \epsilon_0} = \frac{(2.18 \times 10^6 \text{ m/sec})}{z} \frac{Z}{n}
\]

for H-atom,

Radius of 1st orbit, \( r_1 = 0.53 \text{ Å} \)
speed of e in 1st orbit, \( v_1 = 2.18 \times 10^6 \text{ m/sec} \)

Kinetic energy of electron in \( n^{th} \) orbit,

\[
KE = \frac{1}{2} mv^2 = \frac{1}{2} \left( \frac{Ze^2}{2 \epsilon_0 nh} \right)^2
\]

\[
KE_n = \frac{1}{2} \left( \frac{mz^2 e^4}{4 \epsilon_0^2 n^2 h^2} \right) \propto \frac{z^2}{n^2}
\]

Potential energy of electron.
In the electric field of nucleus the PE of electron in \( n^{th} \) orbit is given by

\[
U_n = \left( \frac{1}{4\pi \epsilon_0} \right) \frac{(ze)(-e)}{r}
\]

\[
U_n = -\left( \frac{mz^2 e^4}{4 \epsilon_0^2 n^2 h^2} \right) \propto \frac{z^2}{n^2}
\]

\(-ve\) sign indicates that electron is bound to the nucleus and some work in required to separate it from the nucleus.

Expression for total energy of electron in \( n^{th} \) orbit,

\[
E_n = KE_n + U_n = -\frac{1}{2} \left( \frac{mz^2 e^4}{4 \epsilon_0^2 n^2 h^2} \right) \propto \frac{z^2}{n^2}
\]

If we observe the relations carefully

then \( E_n = -KE_n = \frac{U_n}{2} \)

Putting values of all the constants,
we get

\[ E_n = (-13.6 \times 1.6 \times 10^{-19} \text{ Joule}) \frac{Z^2}{n^2} \]

\[ E_n = -(13.6 \text{ ev}) \frac{Z^2}{n^2} \]

So \[ KE_n = +(13.6 \text{ ev}) \frac{Z^2}{n^2} \] and \[ U_n = (27.2 \text{ ev}) \frac{Z^2}{n^2} \]

From the general expression of total energy

\[ E_n = -\left[ \frac{me^4}{8 \varepsilon_0^2 \hbar^2 c} \right] \hbar c \left( \frac{Z^2}{n^2} \right) \]

or \[ E_n = -(R\hbar c) \frac{Z^2}{n^2} \]

Where \[ R = \frac{me^4}{8 \varepsilon_0^2 \hbar^3 c} \] is called Rydberg constant

\[ R = 1.097 \times 10^7 \text{ m}^{-1} \]

'Rhc' is called 1 Rydberg energy = 13.6 ev.

**Energy levels of hydrogen atom** (\( z = 1 \))

<table>
<thead>
<tr>
<th>( n )</th>
<th>( E_n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(-13.6 \text{ ev})</td>
</tr>
<tr>
<td>2</td>
<td>(-10.2 \text{ ev})</td>
</tr>
<tr>
<td>3</td>
<td>(-6.8 \text{ ev})</td>
</tr>
<tr>
<td>4</td>
<td>(-4.5 \text{ ev})</td>
</tr>
<tr>
<td>5</td>
<td>(-2.4 \text{ ev})</td>
</tr>
</tbody>
</table>

Students are advised to remember these rules for H-atom.

**Note:**

(i) **Binding Energy of a state**: Energy require to remove electron from a particular quantum state is called BE of a that particular state.

eg. BE of \( e^- \) of H-atom in \( n = 4 \) level is \( 0.85 \text{ ev} \)

BE of 1st excited state of H-atom is \( 3.4 \text{ ev} \)

BE of 1st excited state of He\(^+\)-atom is \( 13.6 \text{ ev} \)

(ii) **Ionisation energy**

The energy required to remove an electron from ground state of the atom is called its ionisation energy.

eg. Ionisation energy of H-atom \( = 13.6 \text{ ev} \)

Ionisation energy of He\(^+\) \( = 54.4 \text{ ev} \)
Ionisation energy of H-like atom = $(13.6) \times z^2$ ev

(iii) Ionisation Potential

The Potential difference through which an $e^-$ must be accelerated to acquire this much energy (i.e. ionisation energy) is called ionisation potential.

e.g. Ionisation Potential of H-atom = 13.6 vol

\[ \text{Ionisation Potential} = \frac{\text{Ionisation energy}}{e} \]

(iv) Excitation energy: The energy which must be provided to the $e^-$ of an atom so that it may go to a higher energy level is called excitation energy of that particular excited state.

for equation for H-atom,

Excitation energy of 1st excited state

\[ \Delta E_1 = E_2 - E_1 \]
\[ = (-3.4) - (13.6) \]
\[ = 10.2 \text{ ev} \]

Excitation energy of 2nd excited state

\[ \Delta E_2 = E_3 - E_1 \]
\[ = (-1.51) - (13.6) \]
\[ = 12.09 \text{ ev} \]

Excitation energy of 3rd excited state

\[ \Delta E_3 = E_4 - E_1 \]
\[ = (-0.85) - (13.6) \]
\[ = 12.75 \text{ ev} \]

and so on.

(v) Excitation Potential:

The Potential difference through which an $e^-$ must be accelerated to acquire this much energy (i.e. excitation energy) is called excitation potential.

\[ \text{Excitation Potential} = \frac{\text{Excitation energy}}{e} \]

Illustration:

Find dependency of following physical quantities related with electron revolving in an orbit on Quantum number 'n' and on Atomic Number 'Z':

(a) Equivalent current in $n^\text{th}$ orbit
(b) Time period in $n^\text{th}$ orbit
(c) Angular speed in $n^\text{th}$ orbit
(d) Magnetic field at center due to revolving $e^-$
(e) Magnetic moment due to equivalent current.

Sol. Equivalent current is charge crossing a point in unit time

\[ i = \frac{e}{T} = \frac{ev}{2\pi n^2} \propto \frac{n^2}{z^2} \]

Time period (T) = \[ \frac{2\pi r}{v} \propto \frac{n^3}{z^2} \]
Angular speed ($\omega$) = \( \frac{v}{r} = \frac{2\pi}{T} \times \frac{z^2}{n^2} \)

\( \vec{B} \) at center of coil (\( \vec{B} \)) = \( \frac{\mu_0 i}{2r} \times \frac{i}{r} \times \frac{x}{n^2} \)

Magnetic moment (\( \vec{\mu} \)) = \( iA = i(\pi r^2) \times ir^2 \times n \)

**Illustration:**

Which level of the doubly ionized lithium has the same energy as the ground state energy of the hydrogen atom. Find the ratio of the two radii of corresponding orbits.

**Sol.**

When excited atom makes transition from \( n = n \) to \( n = 2 \)

\[
13.6 z^2 \left[ \frac{1}{z^2} - \frac{1}{n^2} \right] = 10.2 + 17 = 27.2 \text{ ev}
\]

When excited atom makes transition from \( n = n \) to \( n = 3 \)

\[
13.6 z^2 \left[ \frac{1}{z^2} - \frac{1}{n^2} \right] = 4.25 + 5.95 = 10.2 \text{ ev}
\]

Solving the above expression : \( z = 3, n = 6 \)

**Illustration:**

**Difference between \( n^{th} \) and \((n+1)^{th}\) Bohr's radius of H-atom is equal to its \((n-1)^{th}\) Bohr's Bohr's radius, find the value of \( n \).**

**Sol.**

Given

\[
r_{n+1} - r_n = r_{n-1}
\]

(0.53) = \( \frac{(n+1)^2}{z} - 0.53 \frac{(n)^2}{z} = (0.53) \frac{(n-1)^2}{z} \)

\( (n+1)^2 - n^2 = (n - 1)^2 \)

Solving we get \( n = 4 \)

**Illustration:**

A single electron orbits a stationary nucleus of charge Ze where \( Z \) is a constant and \( e \) is the electronic charge. It requires 47.2eV to excite the electron from the 2nd Bohr orbit to 3rd Bohr orbit. Find

(i) the value of \( Z \).

(ii) energy required to excite the electron from the third to the fourth orbit

(iii) the wavelength of radiation required to remove the electron from the first orbit to infinity

(iv) the kinetic energy, potential energy and angular momentum in the first Bohr orbit

(v) the radius of the first Bohr orbit.
**Sol.** We can find difference of energy of \( n = 2 \) and \( n = 3 \) as \( E_3 - E_2 = 47.2 \)

\[
(13.6 \ z^2 \left[ \frac{1}{4} - \frac{1}{9} \right] = 47.2
\]

\( z = 5 \)

Energy required to excite from \( n = 3 \) to \( n = 4 \), \( \Delta E = E_4 - E_3 = 13.6 \ (5)^2 \left[ \frac{1}{9} - \frac{1}{16} \right] = 16.5 \text{ ev} \)

Ionization energy = 13.6 \ (z)^2 = 13.6 \ (5)^2 = 340 \text{ ev} \)

Corresponding wavelength of photon = \[
\frac{12400}{340} \ \text{Å} = 36.5 \ \text{Å}
\]

In first Bohr orbit : \( n = 1 \)

\( KE_1 = 340 \text{ ev} \)

\( PE_1 = -680 \text{ ev} \)

\( E_1 = -340 \text{ ev} \)

Radius of 1st Bohr orbit, \( r_1 = \frac{(0.53)n^2}{z} = \frac{0.53}{5} = 0.106 \text{Å} \)

**Illustration:**

Imagine a hypothetical atom in which mass of electron is 'm' but charge of e becomes -3e. Assuming all other Parameters to be same compare the radius of 1st orbit this hypothetical atom an H-atom. Also find ratio of speed of this e- in n-orbit with that of e- of H-atom.

**Sol.** Radius \( r_n \propto \frac{1}{e} \) for H-atom hence radius of 1st orbit of this hypothetical atom will be one-third of that found for H-atom.

\( v_n \propto e \) for H-atom

\( v_n' \propto 3e \) for Given atom

Hence \( \frac{v_n'}{v_n} = 3 \)

**Practice Exercise**

Q.1 Find the maximum Coulomb force that can act on the electron due to the nucleus in a hydrogen atom.

Q.2 A hydrogen atom emits ultraviolet radiation of wavelength 102.5 nm. What are the quantum numbers of the states involved in the transition?

Q.3 (a) Find the first excitation potential of He⁺ ion. (b) Find the ionization potential of Li⁺⁺ ion.

Q.4 Average lifetime of a hydrogen atom excited to \( n = 2 \) state is \( 10^4 \) s. Find the number of revolutions made by the electron on the average before it jumps to the ground state.

Q.5 Radiation coming from transitions \( n = 2 \) to \( n = 1 \) of hydrogen atoms falls on helium ions in \( n = 1 \) and \( n = 2 \) states. What are the possible transitions of helium ions as they absorb energy from the radiation?
Q.6 A beam of monochromatic light of wavelength \(\lambda\) ejects photoelectrons from a cesium surface \((\phi = 1.9\text{ eV})\). These photoelectrons are made to collide with hydrogen atoms in ground state. Find the maximum value of \(\lambda\) for which (a) hydrogen atoms may be ionized, (b) hydrogen atoms may get excited from the ground state to the first excited state and (c) the excited hydrogen atoms may emit visible light.

**Answers**

<table>
<thead>
<tr>
<th>Q.1</th>
<th>8.2 \times 10^{-4} \text{ N}</th>
<th>Q.2</th>
<th>1 and 3</th>
<th>Q.3</th>
<th>(a) 40.8 \text{ V}</th>
<th>(b) 122.4 \text{ V}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q.4</td>
<td>8.2 \times 10^4</td>
<td>Q.5</td>
<td>(n = 2) to (n = 3) and (n = 2) to (n = 4)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Q.6</td>
<td>(a) 80 \text{ nm}</td>
<td>(b) 102 \text{ nm}</td>
<td>(c) 89 \text{ nm}</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Excitation of atom**

If we provide energy to the electron of atom then there is a possibility that it is excited to higher energy level.

This process can be done in two ways:

- By Absorption of photons
- By collision with other atoms and electrons

**By Absorption of photons**

If an electron is to absorb a photon, the energy \(h\nu\) of photon must be equal to the energy difference \(\Delta E\) between the initial energy level of the electron and a higher level.

It means if we consider the case of H-atom then this atom can absorb only certain specific energy photons which are 10.2 ev, 12.75 ev etc.

The electron of H-atom can not absorb photon of energy 11 ev but this electron can absorb any photon of energy greater than 13.6 eV or more specifically ionization energy of atom. After absorbing energy more than 13.6 eV, rest of the energy may appear as kinetic energy of the free electron.

**Absorption spectrum:**

When an atom absorbs a photon whose energy is exactly equal to the difference of ground state and any of the excited states, this wavelength corresponds line of absorption spectrum.

\[
\text{photons of wavelength } \lambda \rightarrow \text{atom} \rightarrow \text{Absorption spectrum}
\]

**Note:**

- An atom will absorb energy from its ground state only.
- Wavelengths of absorption spectrum can be determined as

\[
\frac{1}{\lambda} = RZ^2 \left( \frac{1}{l^2} - \frac{1}{n^2} \right) \quad n = 2, 3, 4, \ldots
\]

- Number of lines in absorption spectrum between \(n = 1\) and \(n = n\) level will be \((n = 1)\)
By collision with other atoms and electrons
The electron of an atom may also absorb energy during collisions, and may be excited to a higher energy state. During collisions of atoms and electrons the loss of energy must be used to excite the atoms as at atomic level then there is no significance of Thermal energy and rise of temperature. We can not estimate that what type of collision must occur but we can always analyze the possibilities during a collision.
(i) If loss of KE during collision is not sufficient to excite the atom then collision must be perfectly elastic.
(ii) The collision may be inelastic or perfectly inelastic only if loss of KE is exactly equal to any of the excitation energy of the atom.
During a collision maximum loss of KE can be calculated using center of frame, i.e. KE with respect to COM can be lost.

\[
KE_{\text{system,COM}} = \frac{1}{2} \mu V_{\text{rel}}^2
\]

Where \( \mu \rightarrow \) Reduced Mass of system
\(V_{\text{rel}} \rightarrow \) relative velocity of the atoms

Consider an H-atom at rest and a neutron with KE = 25 eV is going to collide with the H-atom. Mass of neutron and H-atom can consider as same.

\[
KE_{\text{max loss}} = \frac{1}{2} \mu V_{\text{rel}}^2
\]

\[
= \frac{1}{2} \left[ \frac{m \cdot m}{m + m} \right] v_0^2
\]

\[
= \frac{1}{2} \text{[KE of neutron]}
\]

\[
= 12.5 \text{ eV}
\]

1st Possibility: Perfectly elastic collision and no excitation
- This is a possible case in every collision if no loss takes place, no excitation to will be there.

2nd Possibility: Inelastic collision, H-atom excited to \( n = 2 \) for this \( \Delta E = 10.2 \text{ eV} \) is required and it is less than \( KE_{\text{max loss}} \) hence a possible case.

3rd Possibility: In elastic collision, H - atom excited to \( n = 3 \) for this \( \Delta E = 12.09 \text{ eV} \) \( KE_{\text{max loss}} \) also possible

4th Possibility: In elastic collision, H-atom excited to \( n = 4 \) for this \( \Delta E = KE_{\text{max loss}} \) not possible

5th Possibility: Perfectly in elastic collision.

In this case \( \Delta E = KE_{\text{max loss}} = 12.5 \text{ eV} \) .... not Possible as 12.5 eV is not an excitation energy.

Note: In all the possibilities, apart from loss rest of the KE will shared by H-atom and neutron. Which can be calculated using momentum - conservation case.

Illustration:
Consider an He\(^+\) - atom at rest, a neutron collision with be atom such that He\(^+\) - atom may be excited to 1st excited state. Find min KE of neutron required.

\[
\text{Sol.} \quad KE_{\text{max loss}} = \frac{1}{2} \mu V_{\text{rel}}^2
\]

\[
= \frac{1}{2} \left[ \frac{m \cdot m}{m + m} \right] v_0^2
\]
\[ \frac{4}{5} [KE \text{ of neutron}] \]

for \( KE_{\text{max loss}} = \Delta E \) (excitation energy)

\[ \frac{4}{5} (KE \text{ of neutron}) = 40.8 \text{ ev} \]

\( KE \text{ of neutron} = 51 \text{ ev} \)

\[ \frac{1}{\lambda} = R_s \left( \frac{1}{4z^2} - \frac{1}{n_z^2} \right) \]

**Note:** The collision of an electron is slightly different from that between atoms and neutrons because the electron is very tiny particles as compared to those hence it penetrates into the atom and can collide with the electron of atom in the ground state. The collision of an electron with the electron of atom will be perfectly elastic hence it may transfer any fraction of its KE to the electron of the atom.

For example, an electron moving with KE = 12 ev can excite the H-atom to 1\textsuperscript{st} excited state by transferring 10.2 ev KE to the electron of H-atom.

Similarly, an electron moving with KE = 15 ev may ionize an H-atom.

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**Practice Exercise**

Q.1 State whether following statements are true/False:
(a) A neutron moving with KE = 20 ev collides with an H-atom at rest. The collision must be perfectly elastic.
(b) A neutron moving with KE = 30 ev collides with an H-atom at rest. The collision may be perfectly inelastic.
(c) An H-atom moving with KE = 25.5 ev collides with another H-atom at rest. The collision may be perfectly inelastic.

Q.2 A neutron having kinetic energy 12.5 eV collides with a hydrogen atom at rest. Neglect the difference in mass between the neutron and the hydrogen atom and assume that the neutron does not leave its line of motion. Find the possible kinetic energies of the neutron after the event.

Q.3 A neutron moving with a speed \( v \) strikes a hydrogen atom in ground state moving towards it with the same speed. Find the minimum speed of the neutron for which inelastic (completely or partially) collision may take place. The mass of neutron = mass of hydrogen = \( 1.67 \times 10^{-27} \) kg.

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**Answers**

Q.1 (a) T (b) T (c) T  Q.2 zero  Q.3 \( 3.13 \times 10^4 \) m/s
de-excitation of atom

Electrons excited to higher energy stay their only for $10^{-8}$ s then they make transition to any lower state by emitting photons and finally come to a ground state. Energy of photons emitted is equal to the difference of energy of the levels. While coming down they may emit photons of various wavelengths which corresponds to several spectral series.

Emission spectrum:

When an electron in excited state makes a transition to a lower state, a photon is emitted. Collection of these photon wavelengths in called emission spectrum.

Hydrogen atom (or hydrogen like hydrogen atoms) consists of only one electron but we get a number of spectral lines in its spectrum (emission).

1. **Lyman series**: The spectral lines of this series correspond to the transition of an electron from some higher energy state to the inner most orbit ($n = 1$ i.e. ground state).

   For Lyman series, $n_1 = 1, n_2 = 2, 3, 4, ...$

   So,
   \[
   \frac{1}{\lambda_{\text{Lyman}}} = R \left( \frac{1}{1^2} - \frac{1}{n_2^2} \right)
   \]

   for hydrogen atom, $Z = 1$

   \[
   \frac{1}{\lambda_{\text{Lyman}}} = R \left( \frac{1}{1^2} - \frac{1}{n_2^2} \right)
   \]

2. **Balmer series**: The spectral lines of this series correspond to the transition of an electron from higher energy state to an orbit having $n = 2$.

   For Balmer serie, $n_1 = 2, n_2 = 3, 4, 5, ...$

   The wave numbers and the wavelengths of spectral lines constituting the Balmer series are given by,

   \[
   \frac{1}{\lambda} = R \left( \frac{1}{2^2} - \frac{1}{n_2^2} \right)
   \]

3. **Paschen series**: The spectral lines of this series correspond to the transition of an electron from some higher energy state to an orbit having $n = 3$.

   For Paschen series, $n_1 = 3, n_2 = 4, 5, 6, ...$

   The wave numbers and the wavelengths of spectral lines constituting the Paschen series are given by,

   \[
   \frac{1}{\lambda} = R \left( \frac{1}{3^2} - \frac{1}{n_2^2} \right)
   \]

   Paschen series is so named because it was discovered by paschen. Just like other series, this series was first predicted by Bohr.

4. **Barcket series**: The spectral line of this series correspond to the transition of an electron from a higher energy state to the orbit having $n = 4$.

   For this serie, $n_1 = 4, n_2 = 5, 6, 7, ...$

   \[
   \frac{1}{\lambda} = R \left( \frac{1}{4^2} - \frac{1}{n_2^2} \right)
   \]
5. **Pfund series**: The spectral line of this series correspond to the transition of an electron from a higher energy state to the orbit having \( n = 5 \).

   For the series, \( n_1 = 5 \) and \( n_2 = 6, 7, 8, \ldots \).
   The wave number and the wavelength of the spectral lines constituting the Pfund series are given by:
   \[
   \frac{1}{\lambda} = R \left( \frac{1}{5^2} - \frac{1}{n^2} \right)
   \]

6. **Humphrey series**: For this series, \( n_1 = 6 \) and \( n_2 = 7, 8, 9, \ldots \).

   For this series, \( n_1 = 6 \) and \( n_2 = 7, 8, 9, \ldots \).
   The wave number and the wave lengths of the spectral lines constituting the Humphrey series are given by:

   ![Diagram of spectral series with energy levels](Image)

   Spectral lines originate in transitions between energy levels.
   Shown are the spectral series of hydrogen. When \( n = \infty \), the electron is free.

**Note:**

- While coming down to ground state a single atom in \( n = n \) state may emit a maximum \((n - 1)\) photons.
- First line of a series corresponds to lowest energy photon emitted e.g. first line of blamer series corresponds to transition from \( n = 3 \) to \( n = 2 \).
- Series limit corresponds to maximum energy photon emitted e.g. series limit of blamer series corresponds to transition from \( n = \infty \) to \( n = 2 \).
- Maximum number of lines in emission spectrum of a gas which is excited to a level \( n = n \) will be \( n(n - 1)/2 \).
- For an atom in quantum state \( n = n \)
  - Max energy photon will be emitted for a transition from \( n = n \) to \( n = 1 \).
  - Min energy photon will be emitted for a transition from \( n = n \) to \( n = n - 1 \).

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Mass of the nucleus is comparable to mass of electron

If mass of the nucleus is comparable to mass of electron, then the electron and nucleus revolve in coplanar concentric circular paths of radii \( r_1 \) and \( r_2 \) about their common centre of mass. The electrostatic force of attraction provides them necessary centripetal force. They revolve with the same angular velocity and their sense of rotation is also same.

From the figure,

\[ r_1 + r_2 = r_n \quad \text{... (i)} \]

and \[ Mv_1 = mv_2 \]

or \[ \frac{r_1}{r_2} = \frac{m}{M} \quad \text{... (ii)} \]

From equation (i) and (ii),

\[ r_1 = \left( \frac{m}{m + M} \right) r_n; \quad r_2 = \left( \frac{m}{m + M} \right) r_n \]

Let their angular velocities be \( \omega_1 \) and \( \omega_2 \) and electrostatic force of attraction between them be \( F \), then,

\[ F = M\omega_1^2 r_1 \quad \text{(for M)} \]

and \[ F = m\omega_2^2 r_2 \quad \text{(for m)} \]

So, \( M\omega_1^2 r_1 = m\omega_2^2 r_2 \) but \( Mr_1 = mr_2 \) [from equation (ii)]

So, \( \omega_1^2 = \omega_2^2 \) or \( \omega_1 = \omega_2 = \omega \) (say)

So they revolve with same angular velocity about their common centre of mass.

Now let us see why 'm' is replaced by the reduced mass \( \mu \) when motion of nucleus is also to be considered. Centripetal force to the electron is provided by the electrostatic force, so,

\[ mr_2\omega^2 = \frac{Ze^2}{4\pi\varepsilon_0 r_n^2} \quad \text{or} \quad \left( \frac{Mm}{M + m} \right) r_n^2 \omega^2 = \frac{Ze^2}{4\pi\varepsilon_0} \]

or \[ \mu r_n^2 \omega^2 = \frac{Ze^2}{4\pi\varepsilon_0} \quad \text{... (iii)} \]

where, \[ \mu = \frac{1}{m} + \frac{1}{M} = \frac{Mm}{M + m} \]

Now, moment of inertia about the common centre of mass,

\[ I = Mr_1^2 + mr_2^2 = M \left( \frac{m}{m + M} \right)^2 Mr_1^2 + mr_2^2 + m \left( \frac{M}{m + M} \right)^2 r_n^2 = \mu r_n^2 \]

According to Bohr's theory of equation of angular momentum,

\[ I\omega = \frac{nh}{2\pi} \quad \Rightarrow \quad \mu r_n^2 \omega = \frac{nh}{2\pi} \quad \text{... (iv)} \]
From equations (iii) and (iv), we get,

$$ r_n = \frac{e_0 n^2 h^2}{\pi \mu e^2 Z} $$

...(v)

Comparing this value with the value of $r$, when nucleus was assumed be massive, we see that, 'm' has been replaced by $\mu$. Further electrical potential energy of the system,

$$ U_n = \frac{Ze^2}{4\pi e_0 r_n} $$

and kinetic energy, $K_n = \frac{1}{2} I \omega^2 = \frac{1}{2} \mu r_n^2 \omega^2$

**Explanation of bohr quantisation rule from de-Broglie's Concept**

Einstein suggested that light behaves both as a material particle as well as wave. de-Broglie extended Einstein's view and said that all forms of matter like electrons, protons, neutrons etc. also dual character. He further said that wavelength ($\lambda$) associated with a particle of mass 'm' moving with velocity 'v' is given by,

$$ \lambda = \frac{h}{mv} = \frac{h}{p} $$

(where $\lambda$ is called de-Broglie's wavelength)

Further: If the K.E. of the moving particle is $K$, then, $\lambda = \frac{h}{\sqrt{2mK}}$

If a charged particle 'q' is accelerated through a potential difference $\Delta V$ then, $\lambda = h \sqrt{2mq(\Delta V)}$

An electron behaves as standing or stationary wave, which extends round the nucleuses in a circular orbit. If the two ends of the electron wave meet to given a regular series of crests and troughs, the electron wave is said to be in phase. i.e. there is constructive interference of electron waves and the electron motion has a character of standing wave or non-energy radiation motion.

Whatever be the path of the electron wave round the nucleus, it is a necessary condition to get an electron wave in phase so that the circumference of the Bohr's orbit (=2$\pi r$) is equal to the whole number multiple to wavelength $\lambda$ of electron wave i.e.

![Circumference](image)

Circumference = 2 wavelengths

Circumference = 4 wavelengths

Circumference = 8 wavelengths

Figure show some modes of vibration of a wire loop. In each case a whole number of wavelengths fit into the circumference of the loop.

$$ 2\pi r = n\lambda \text{ or } \lambda = \frac{2\pi r}{n} $$

...(i)
Where 'n' is a whole number which denotes the number of wavelengths associated with an electron wave extending round the nucleus.

Now according to de - Broglie,

\[ \lambda = \frac{h}{mv} \]  

...(ii)

From equation (i) and (ii) we get,

\[ \frac{2\pi}{n} = \frac{h}{mv} \text{ or } mv = \frac{nh}{2\pi} \]

An electron revolving in a permitted orbit does not radiate energy, through it is accelerating, so the total energy of the electron remains constant. That is why the permitted orbits are also called stationary or non-radiating orbits.

**Energy of a trapped electron**

The energy of a trapped particle is quantized.

The simplest case is that of a particle that bounces back and forth between the walls of a box. We shall assume that walls of the box are infinitely hard, so the particle does not lose energy each time it strikes a wall and that its velocity is sufficiently small so that we can ignore relativistic conditions.

From a wave points of view, a particle trapped in a box is like a standing wave in a string stretched between the box's walls. The possible de-Broglie wavelengths of the particle in the box therefore are determined by the width L of the box. The general formula for the permitted wavelength is given by.

de Broglie wavelengths of trapped particle, \( \lambda_n = \frac{2L}{n}, n = 1,2,3, \ldots \ldots \)

Further for a matter wave de-Broglie wavelength,

\[ \lambda_n = \frac{h}{mv_n} = \frac{h}{\sqrt{2mK_n}} \text{ (where } k_n \text{ is the kinetic energy of the particle)} \]

Comparing the two expressions, we have,

\[ \frac{h}{\sqrt{2mK_n}} = \frac{2L}{n} \text{ or } K_n = \frac{n^2h^2}{8mL^2} \]

Since the particle has no potential energy in this model, the only energies it can have, are,
Particle in a box, \( E_n = \frac{n^2 \hbar^2}{8mL^2} \), \( n = 1, 2, 3, \ldots \).

Each permitted energy is called an energy level and the integer 'n' that specifies an energy level \( E_n \) is called its quantum number.

We can draw three general conclusions from the energy expression of a trapped electron. These conclusions apply to any particle confined to a certain region of space for instance, an atomic electron held captive by the attraction of the positively charge nucleus.

1. A trapped particle can not have an arbitrary energy, as free particle can have.
2. A trapped particle can not have zero energy.
3. Because Planck's constant is so small \( (\hbar = 6.63 \times 10^{-34} \text{ J sec}) \), quantization of energy is conspicuous only when 'm' and L are also small. That is why we are not aware of energy quantization in our own experience.