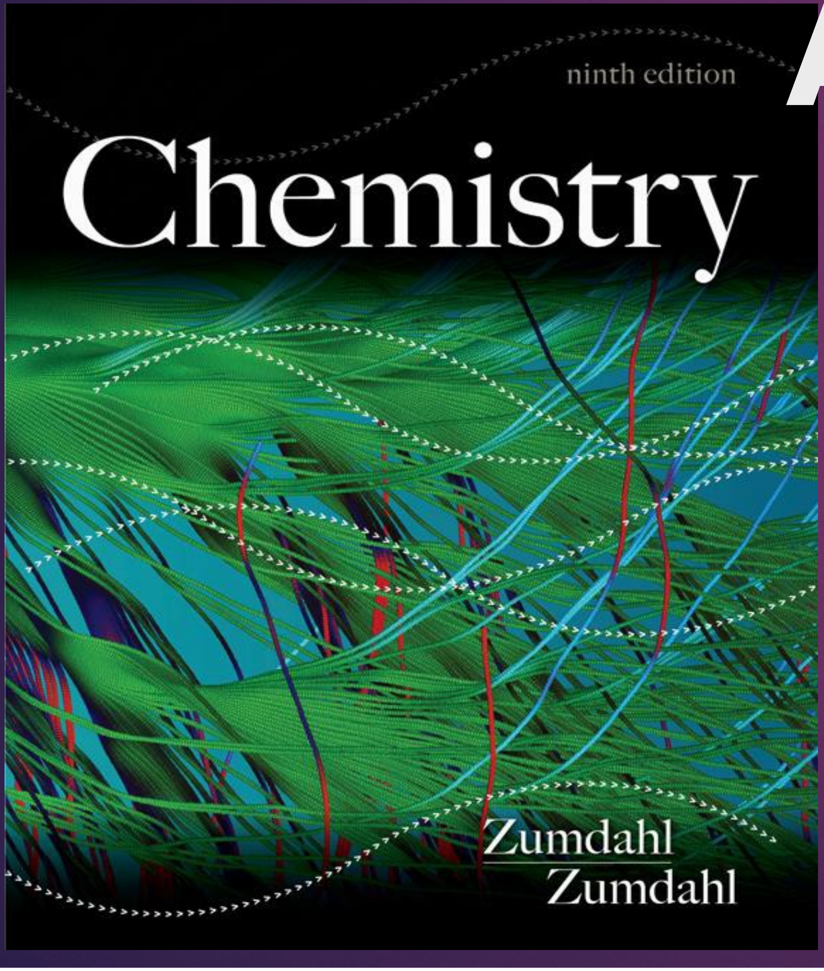
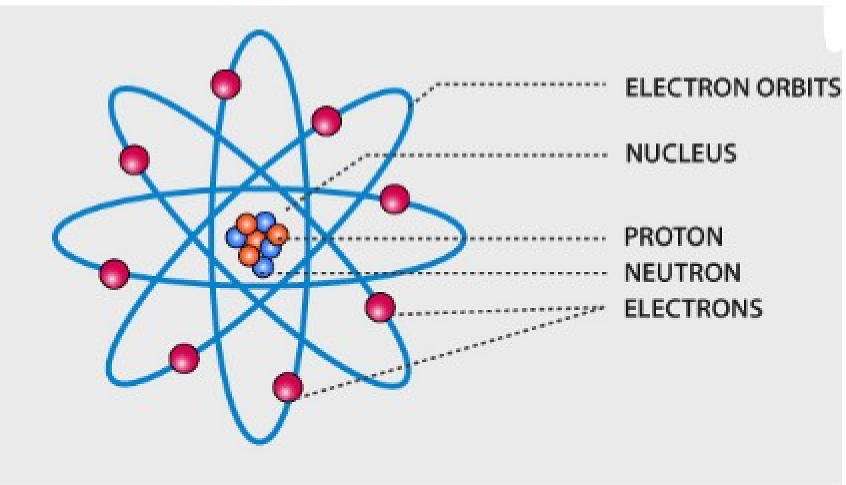


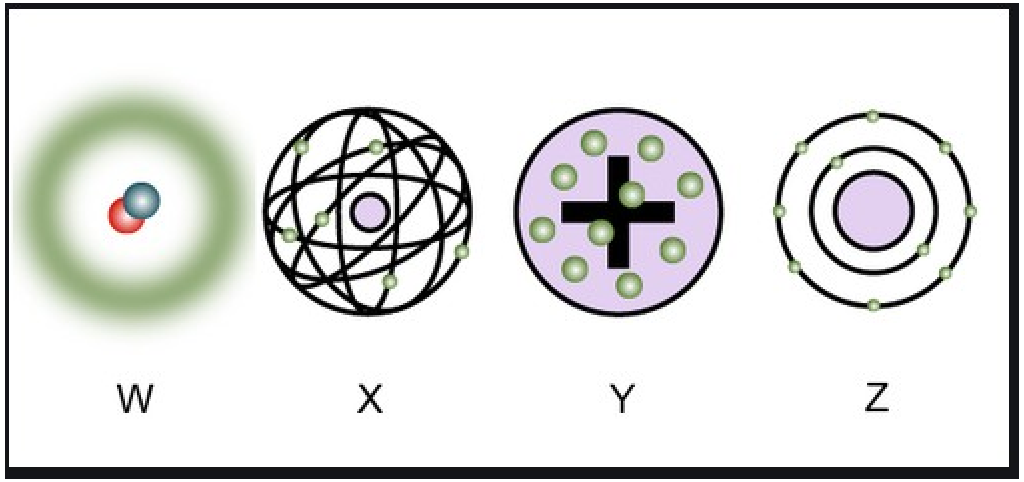
Atomic Structure

continues



Earlier models of an atom

- Once it was established that the atom is not indivisible, the scientists made attempts to *understand the structure of the atom.*
- A # of models were proposed for the internal structure of the atom.
- *The first attempt to describe the structure of atom in terms of a model was made by J.J Thomson.*



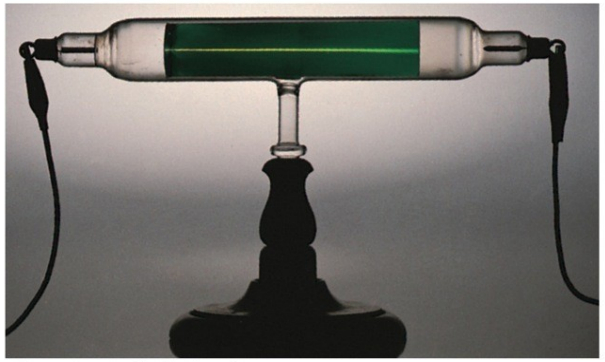
Early Experiments to Characterise the Atom

J. J. Thomson (1898—1903) Atomic Model

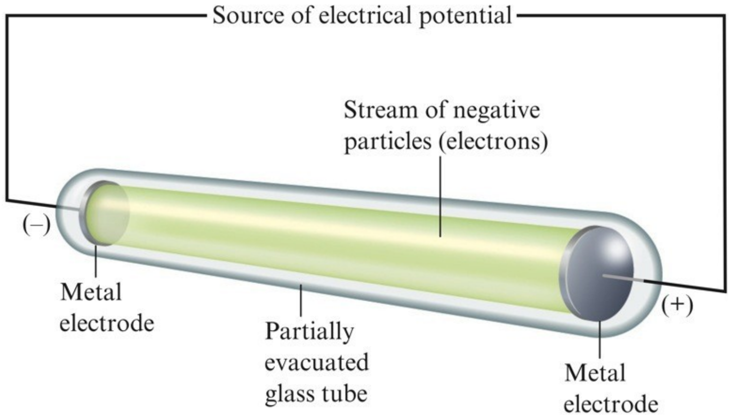
- Postulated the existence of negatively charged particles, that we now call electrons, using **cathode-ray tubes**.
- Determined the charge-to-mass ratio of an electron.
- The atom must also contain positive particles that balance exactly the negati charge carried by electrons….**rendering the atom neutral!**

Joseph John Thomson won the Nobel Prize in 1906 for the discovery of the electron.

Cathode-Ray Tube



Richard Megna/Fundamental Photographs © Cengage Learning



Thomson atomic model

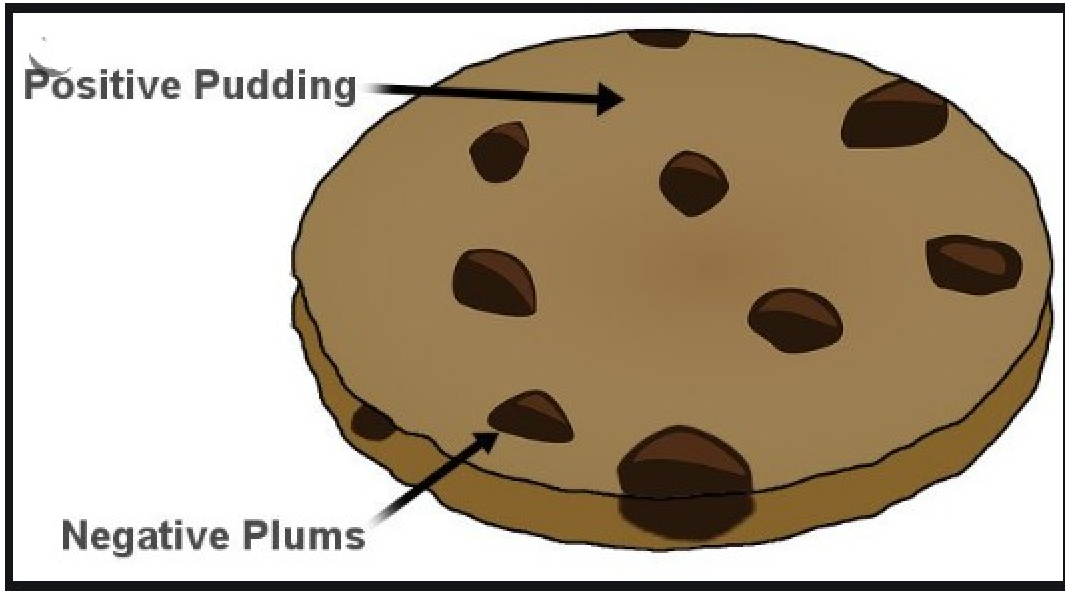
- He discovered the e in *1897*, proposed the ***Plum Pudding Model of the Atom*** *in 1904.*

- *The model was proposed* **before the discovery of the atomic nucleus** in order to include the electron in the atomic model.

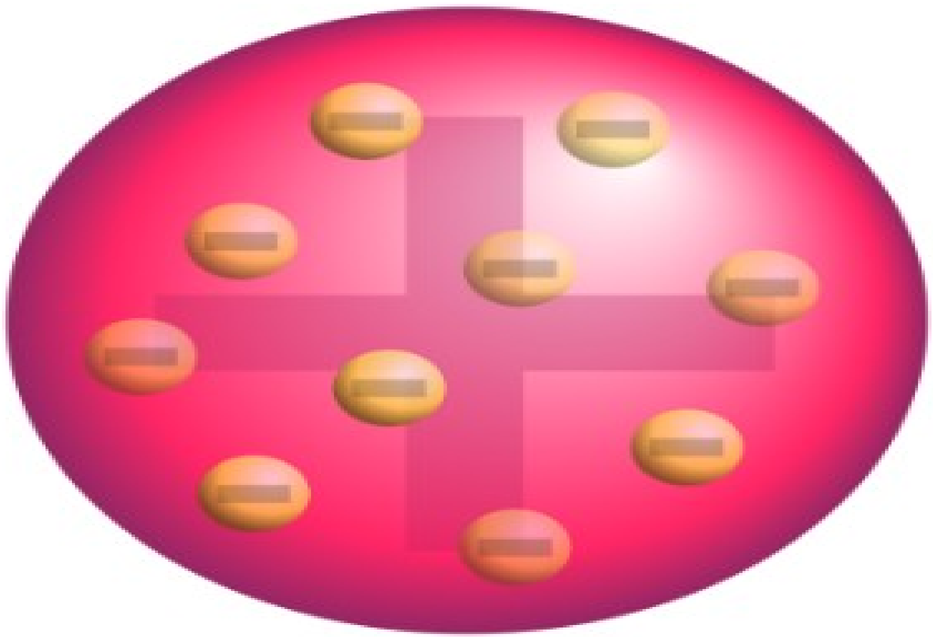
- Proposed that atoms can be considered as a large positively charged body with a # of small negatively charged electrons scattered throughout it.

The Plum Pudding Model

- **it envisaged the atom as a sphere of positive charge, with electrons dotted throughout like plums in a pudding.**



Plum pudding model of the atom



Plum pudding model of the atom: A schematic presentation of the plum pudding model of the atom; in Thomson's mathematical model the "corpuscles" (in modern language, electrons) were arranged non-randomly, in rotating rings.

Thomson atomic model

- Though several alternative models were advanced in the 1900s…

- Thomson held that atoms are uniform spheres of postively charged matter in which electrons are embedded.

- Abandoned (1911) on both theoretical & experimental grounds in favour of the

Robert Millikan (1909)

- Performed experiments involving charged oil drops.
- Determined the magnitude of the charge on a single electron.
- Calculated the mass of the electron

  (9.11×10^{-31} kg).

Henri Becquerel (1896)

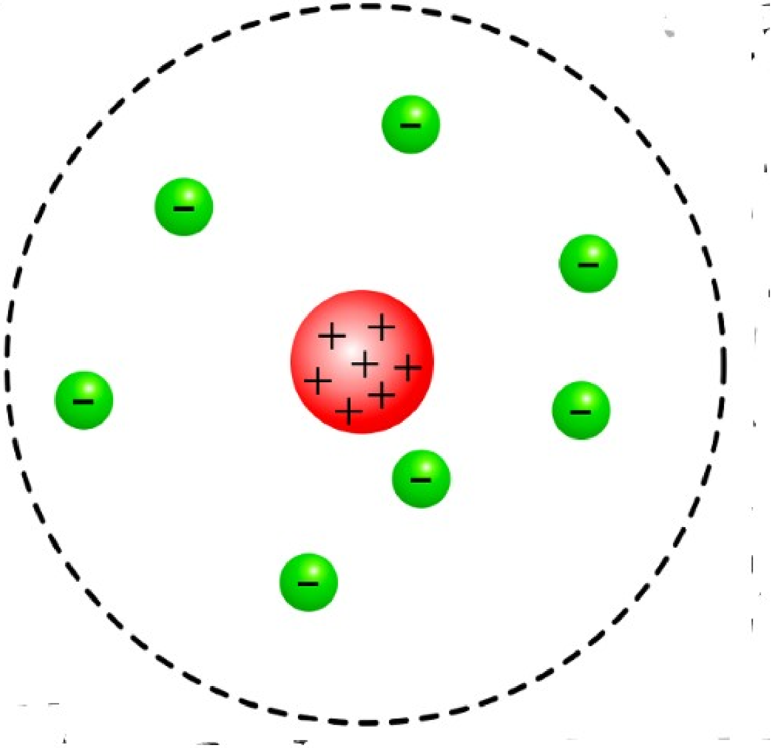
- Discovered radioactivity by observing the spontaneous emission of radiation by uranium.
- Three types of radioactive emission exist:
  - Gamma rays (ϒ) – high energy light
  - Beta particles (β) – a high speed electron
  - Alpha particles (α) – a particle with a 2+ charge

Rutherford atomic model

- AKA *nuclear atom* or *planetary model of the atom.*
- is description of the structure of atoms proposed (1911) by the New Zealand-born physicist Ernest Rutherford.
- model described the atom as a tiny, dense, +vely charged core called a nucleus.

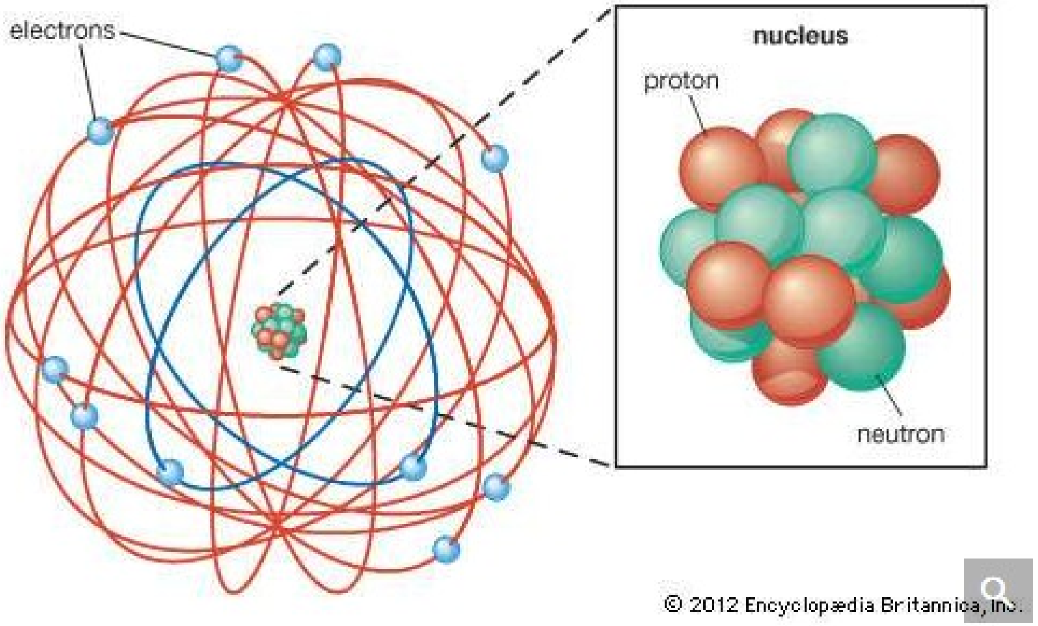
Rutherford atomic model

- The model shows an atom as an **empty space** where electrons orbit a positively charged fixed nucleus in a predictable & set paths.
- He researched extensively on radioactivity..
  - & won the Nobel Prize for his discoveries in 1908.
- It was then that he started developing the model of the atom.



Rutherford atomic model

- **Mass of an atom is concentrated in the nucleus.**
- **Around the nucleus are light negative constituents, called electrons,.**
- **Electrons circulate at some distance, much like planets revolving around the Sun.**



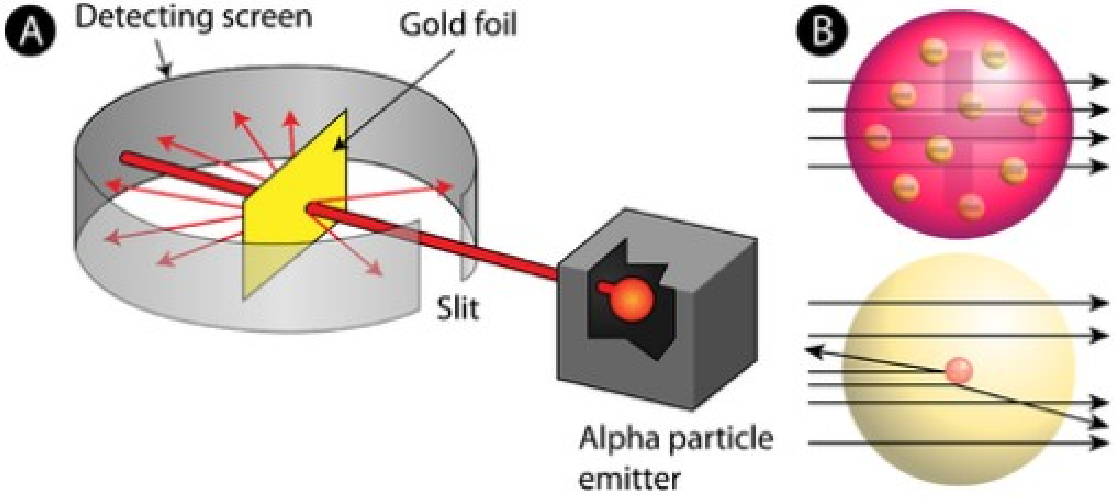
© 2012 Encyclopædia Britannica, Inc.

Rutherford’s Experiment

- Performed an experiment called ‘*Gold Foil Experiment’ or ‘α- ray scattering experiment*’ to test the structure of an atom as proposed by Thomson.
- These results led Rutherford to conclude that:

- ✓ The atom contained some dense & positively charged region located at the center of the atom that he called as *nucleus.*

Rutherford atomic model



(A) A radioactive element that emitted alpha particles was directed toward a thin sheet of gold foil that was surrounded by a screen which would allow detection of the deflected particles.

(B) According to the plum pudding model (top) all of the alpha particles should have passed through the gold foil with little or no deflection.

Rutherford found that a small percentage of alpha particles were deflected at large angles, which could be explained by an atom with a very small, dense, positively-charged nucleus at its center (bottom).

Rutherford’s Atomic Model

- Rutherford proposed that an atom has a positively charged core (nucleus) surrounded by the negative electrons.

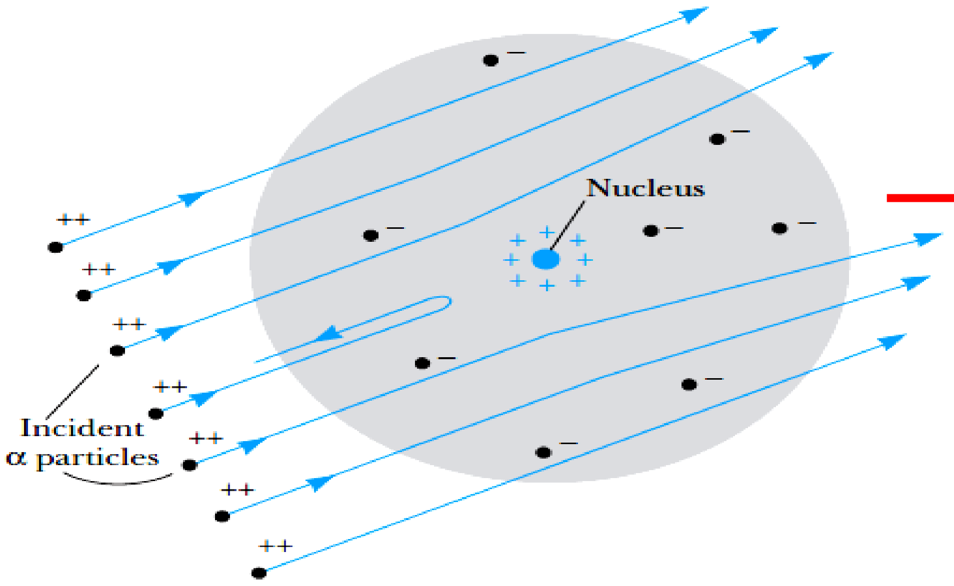
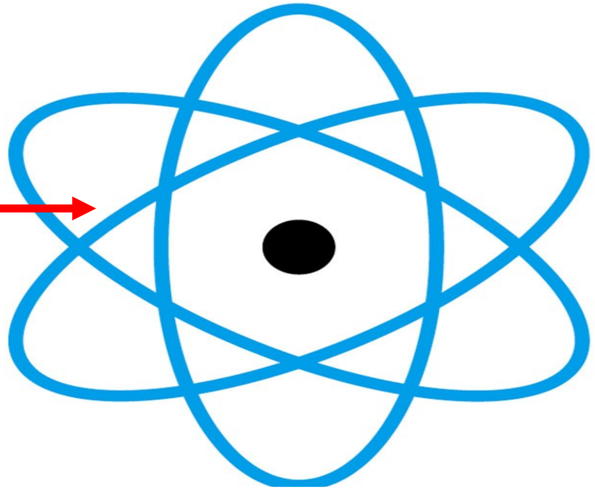


Figure 4.11 Scattering of α particles by a dense, positively charged nucleus.



Something 3-D where there is a particle nucleus and particle electrons in certain orbits, not correct

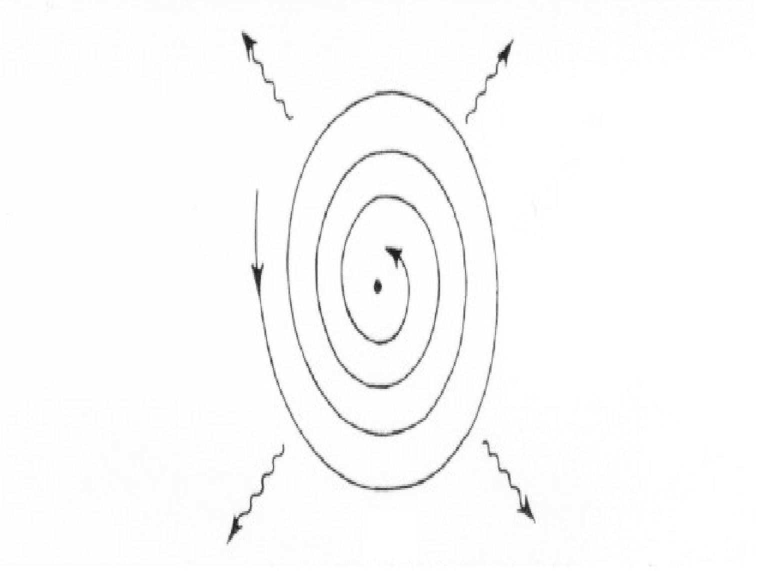
Rutherford’s conclusion

- ✓ All the positive charge of the atom & most of its mass was contained in the nucleus.
- ✓ Nucleus occupies a very small volume relative to the volume of the atom.
- ✓ The rest of the atom must be empty space which contains the much smaller & -vely charged e *undergoing continuous random acceleration*.

Rutherford’s Experiment

Main problem with this theory:

- According to the Maxwell’s theory of electromagnetic radiation, a charged particle undergoing acceleration would continuously emit radiation and lose energy.
- Since the electron in the atom is also a charged particle & is under acceleration, it is expected to continuously lose energy.
- As a consequence, the e moving around the nucleus would approach the nucleus by a spiral path & the atom would collapse.



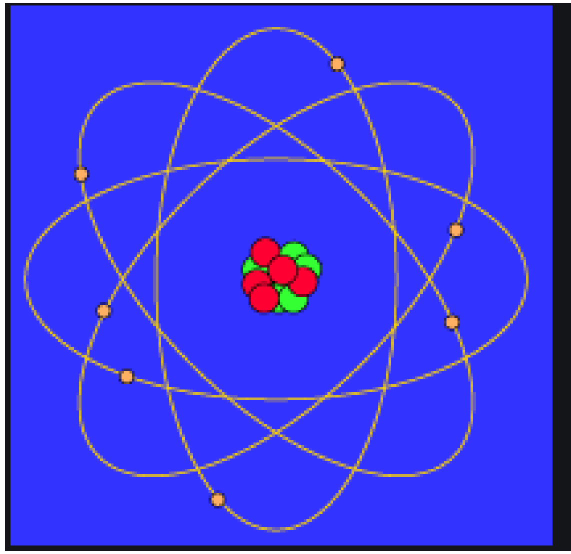
According to classical physics, an electron in orbit around an atomic nucleus should emit electronmagnetic radiation (photons) continuously, because it is continually accelerating in a curved path. The resulting loss of energy implies that the electron should spiral into the nucleus in a very short time (i.e. atoms can not exist).

Rutherford’s Experiment

- Since the atom doesn't’ collapse, the Rutherford’s model *failed to explain the stability of the atom.*
- Rutherford’s model proved to be an important step towards a full understanding of the atom.
- However, it did not completely address the nature of the electrons & the way in which they occupied the vast space around the nucleus
- The next attempt to suggest a model for atom was made by Neils Bohr- **a student of Rutherford.!!**

Bohr’s model of an atom

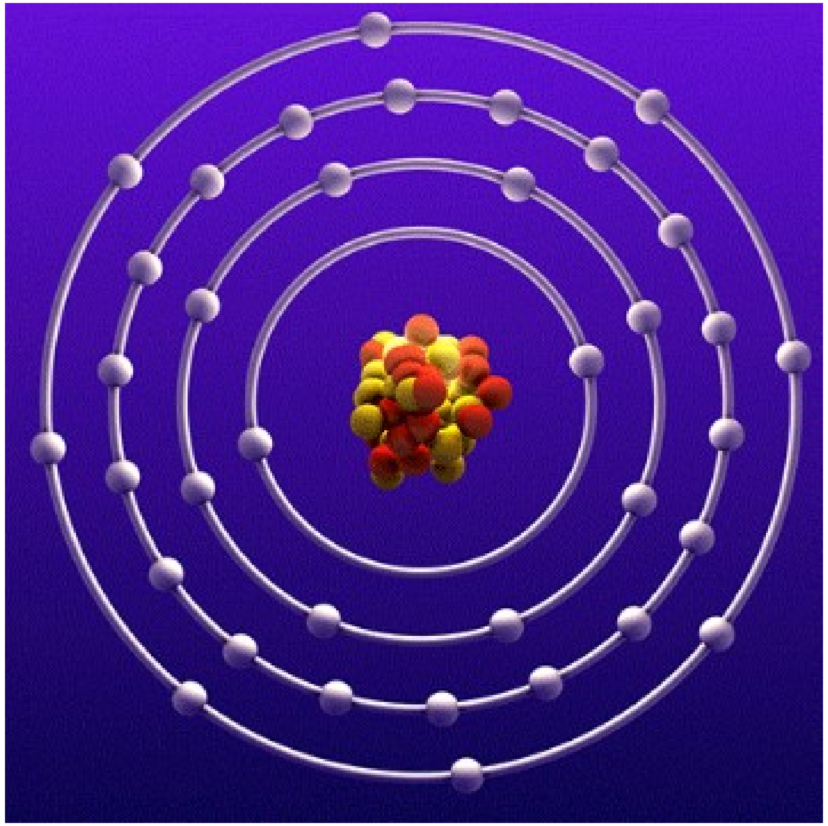
- **Bohr model**, description of the structure of atoms, especially that of hydrogen, proposed (1913).
- In this model *e* moves around the nucleus in **circular paths-**..
- **Model similar in structure to the Solar System but with attraction provided by electrostatic forces rather than gravity.**



Bohr’s model of an atom

- He **modified** the Rutherford model by requiring that the electrons move in *orbits of fixed size & energy i.e they are quantized.*

- When something is quantized, it means that only specific values are allowed.



Bohr model

- **He explained why the e isn't pulled into the nucleus (stability of an atom) & why H atom only** *emits certain wavelength of light.*

- Niels Bohr used Planck's theories to develop a *new* & *more accurate model of the atom.*

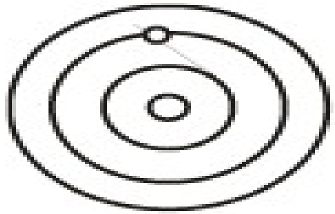
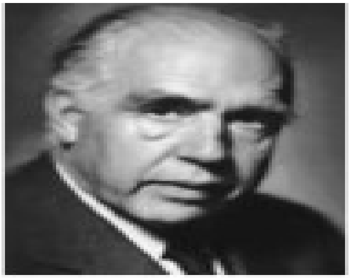


Fig. 3.10: *Bohr's model*



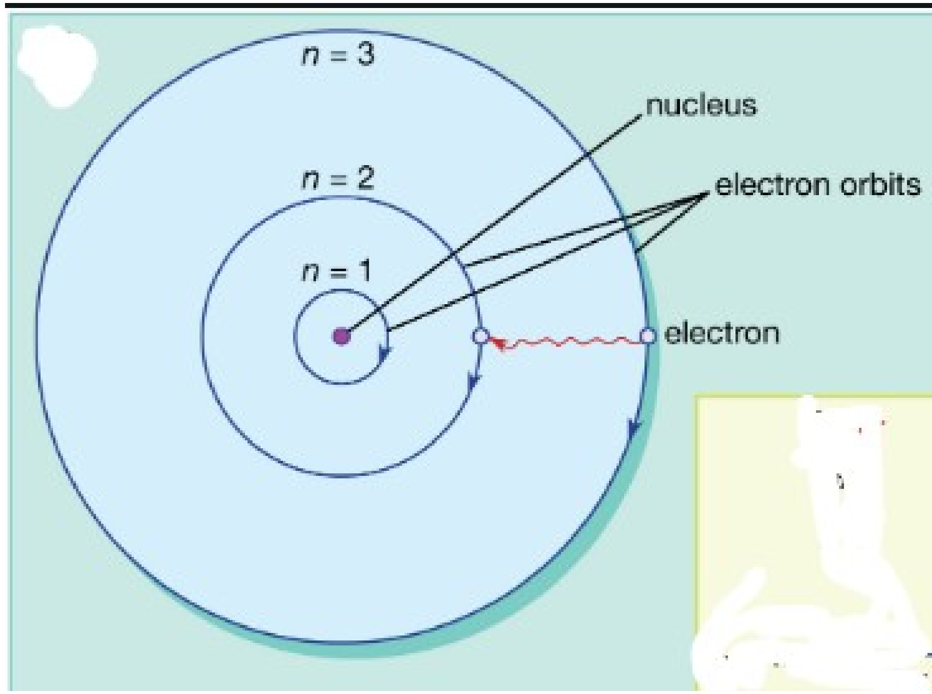
Bohr won the Nobel Prize in Physics in 1922 for his work.

Bohr model

- The Bohr model is a relatively primitive model of the H atom, compared to the *valence shell atom*.
- However, because of its simplicity, &its correct results for selected systems,..
- … the Bohr model still commonly taught to introduce students to quantum mechanics or energy level diagrams before moving on to the more accurate, but more complex, valence shell atom!!

Bohr model

- In order to explain the **stability of an atom**, Neils Bohr gave a new arrangement of electrons in the atom.
- According to him, e could revolve around the nucleus in only '*certain orbits*' (*energy levels*).
- each orbit has a different radius.!!

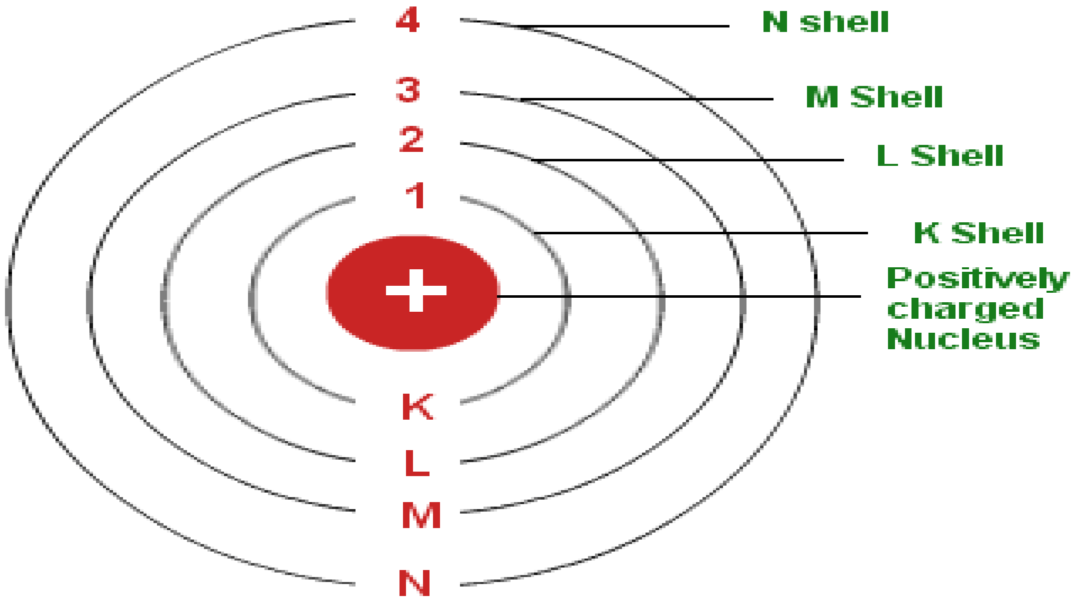


Bohr model

- The *fixed circular* paths are called *energy levels or shells* or orbits or stationary orbits.

- The energy levels are represented in 2 ways: either by the numbers 1, 2, 3, 4, 5 & 6 or by letters K, L, M, N, O & P.

Bohr model



Arrangement of energy levels around the nucleus

- ❑*can show how many e can be present in each electron shell or orbit.!!*

Bohr model

- The energy levels are counted from center outwards.

- Each energy level is associated with a *fixed amount of energy.*

- The shell nearest to the nucleus has minimum energy & the shell farthest from the nucleus has maximum energy.

The Bohr model

- *Niels Bohr was coupling the Rutherford postulation & the Max Planck quantum theory,..*
- … proposed that the atom consists of a +vely charged nucleus of protons & neutrons..
- …. surrounded by -vely charged e traveling in discrete orbits at a fixed distance from the nucleus.
- An e has a discrete or specific quantity of energy (E) which is called as quantum.

Postulates of the Bohr atomic model

- ☐ Bohr's atomic model is built upon a set of postulates, which are as follows (Salient features of Bohr's atomic model):

1. The electrons move in definite circular paths around the nucleus.

- ✓ called these circular paths as orbits & postulated that as long as the e is in a given orbit its energy does not change (or energy remains fixed).
- ✓ These orbits were therefore referred to as stationary orbits or stationary states or non radiating orbits.

Postulates of the Bohr atomic model

- ✓ Electrons revolve around the nucleus in stable orbits without emission of radiant energy.
- ✓ Each orbit has a definite E & is called E shell or E level.
- ✓ Each orbit has a certain energy associated with it i.e., only certain values of energy are possible.
- ✓ Based on this, the energy of an e is said to be **quantized.**

Postulates of the Bohr atomic model

2. The electron can change its orbit by *absorbing or releasing energy*.

- ✓ An e at a lower (initial) state of energy, E_i can go to a (final) higher state of energy, E_f by absorbing a single photon of energy given by:

$$E = h\nu = E_f - E_i$$

$$\Delta E = E_{\text{final state}} - E_{\text{initial state}}$$

Postulates of the Bohr atomic model

- Similarly, when an e changes its orbit from a higher initial state of energy E_i to a lower final state of energy E_f, a single photon of energy hν is released.
- This is called *Bohr's frequency condition*

Fig. 3.11 : *Absorption and emission of photon causes the electron to change its energy level.*

Postulates of the Bohr atomic model

- The E of an e changes only when it moves from one orbit to another. !!

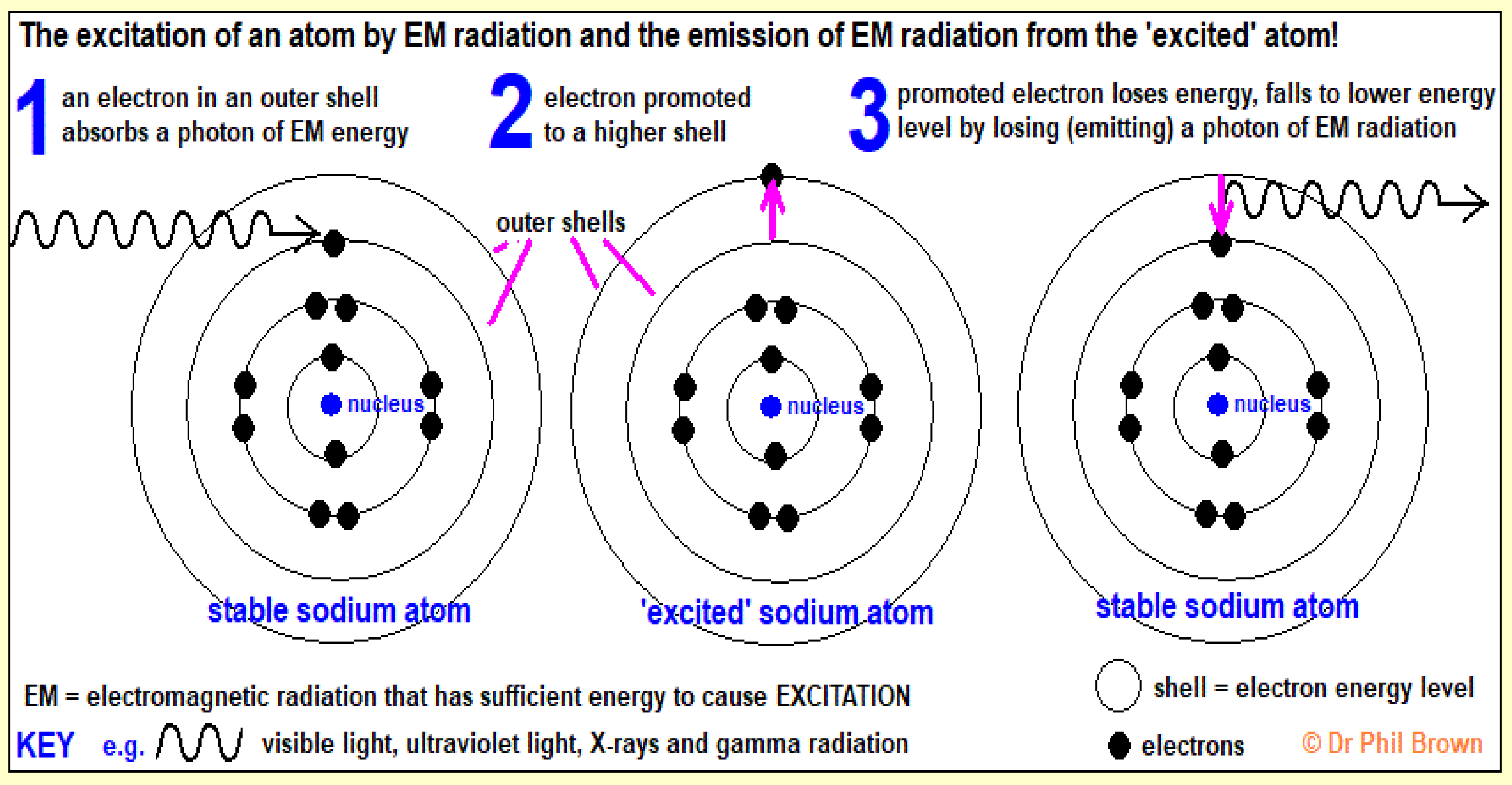
- An electronic transition from an inner orbit to outer orbit involves *absorption of energy*.

- Similarly, when an e jumps from an outer orbit to inner orbit it releases energy, which is equal to the difference between the two energy levels.

Postulates of the Bohr atomic model

- **Ground State**: The lowest possible energy state for an atom…No e has moved to a higher energy level.

- When in a higher level it is in an **Excited state…can only occur if atom is exposed to Energy.!!**



The excitation of an atom by EM radiation and the emission of EM radiation from the 'excited' atom!

1 an electron in an outer shell absorbs a photon of EM energy

2 electron promoted to a higher shell

3 promoted electron loses energy, falls to lower energy level by losing (emitting) a photon of EM radiation

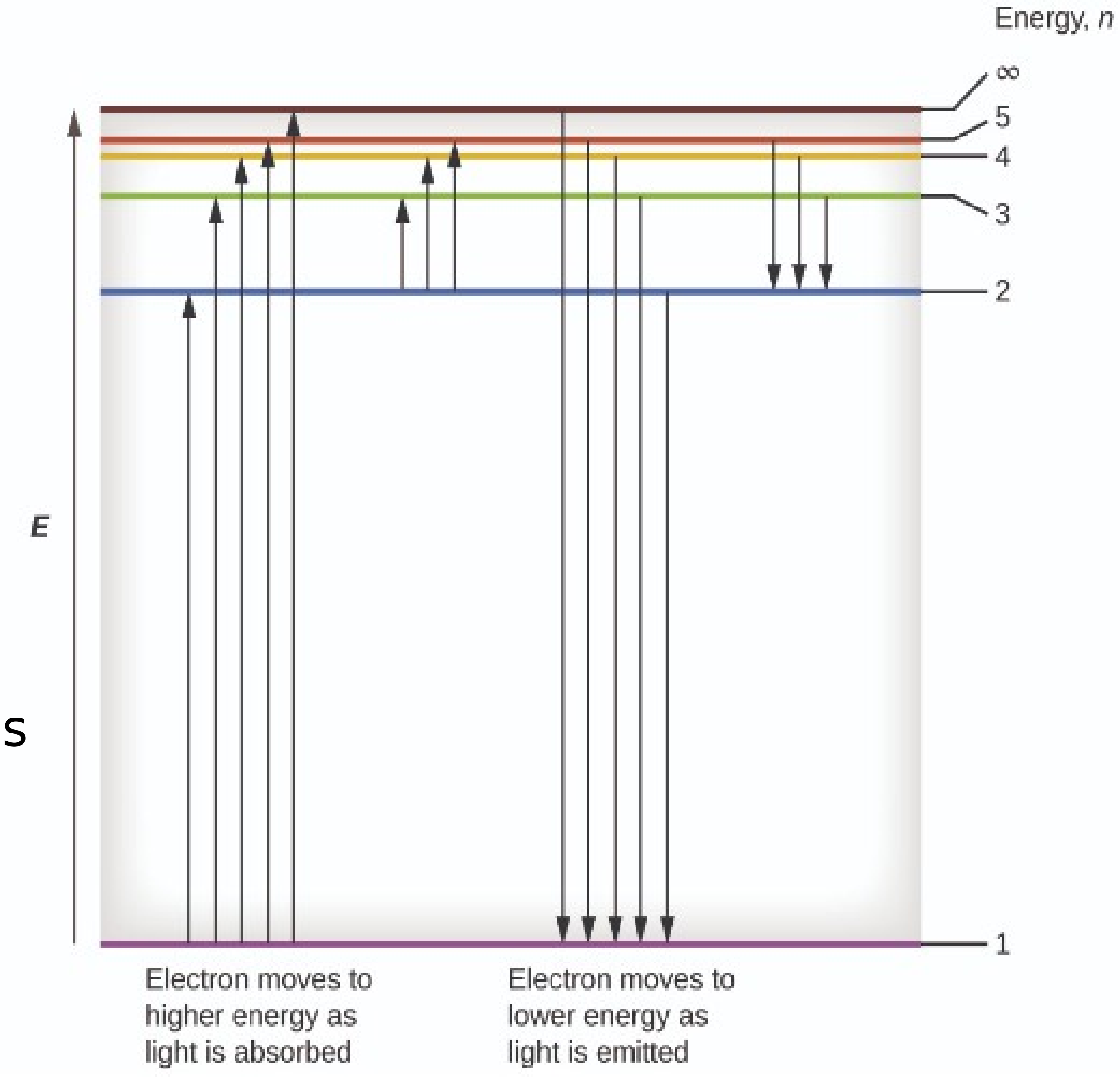
EM = electromagnetic radiation that has sufficient energy to cause EXCITATION

KEY e.g. visible light, ultraviolet light, X-rays and gamma radiation

Electronic Transitions in the Bohr Model for the Hydrogen Atom

- **An Energy-Level Diagram for Electronic Transiti**

  - The horizontal lines show the **relative E** of orbits in the Bohr model of the H atom.
  - The vertical arrows depict the E of photons absorbed (left) or emitted (right) as electrons move between these orbits.



Postulates of the Bohr atomic model

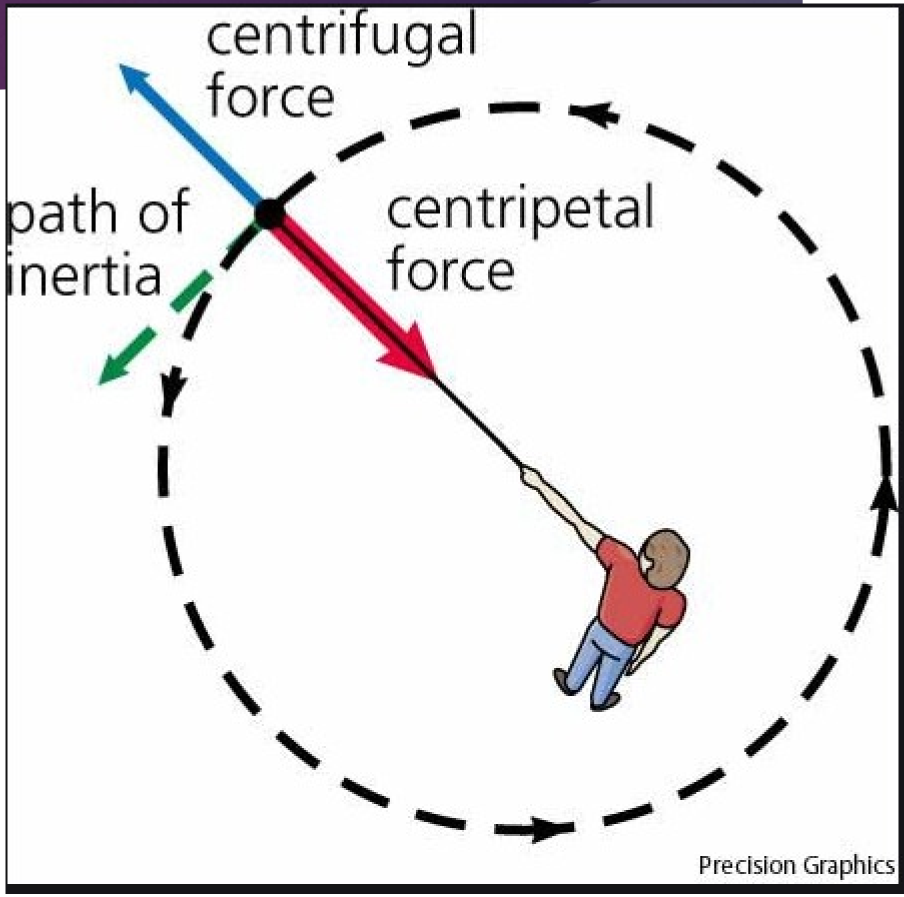
3. The different energy levels are denoted by integers such as n=1 or n=2 or n=3 & so on.

- These are called as **quantum numbers.**

- The range of quantum number may vary and begin from the lowest energy level (nucleus side n=1) to highest energy level.

Bohr atomic model

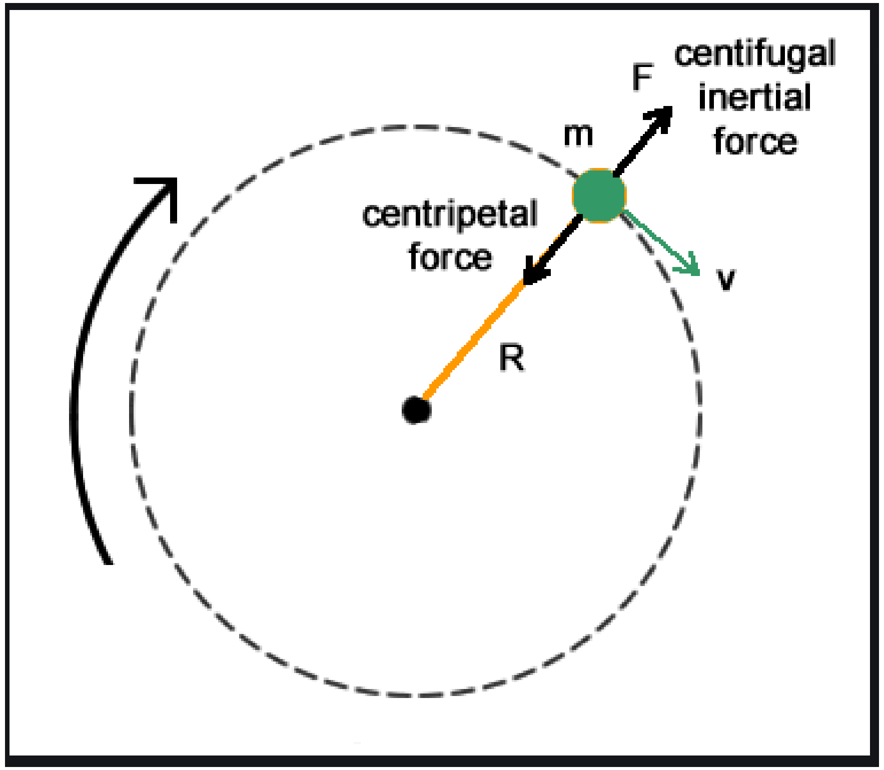
- **Stability of an atom:**
- Explained based on **centripetal force & centrifugal force,** action-reaction force pair associated with circular motion



Precision Graphics

Bohr atomic model

- The attraction force between e & nucleus is balanced by centrifugal force of electron & the electrostatic forces between the nucleus & +ve nucleus!
- Centrifugal force is due to motion of electron and tend to take electron away from nucleus.
- **Centripetal force is the** electrostatic forces between the nucleus & +ve nucleus!



Bohr atomic model

- Bohr came up with an equation that describes the energy of an electron in the H atom:

$$E = -2.178 \times 10^{-18}\,\mathrm{J}\left(\frac{Z^2}{n^2}\right)$$

$$E = -\frac{b}{n^2} \quad \text{where the constant } b = 2.18 \times 10^{-18}\,\mathrm{J}$$

- n is an integer (the larger the value of n, the larger is the orbit radius) & Z is the nuclear charge
- *n* = principal quantum number = orbit number

Bohr atomic model

- The energies of the Bohr orbits are inversely proportional to the square of the quantum number n.

- As n increases the value of the energy increases (becomes lesser negative or more positive).

- It means that as we go farther from the nucleus the energy of the orbit goes on increasing.

Bohr atomic model

- *The -ve sign indicates that the E of an e bound to the nucleus is lower than that of an e at infinite distance given by:*

$$E = -2.178 \times 10^{-18}\,\mathrm{J}\left(\frac{Z^2}{\infty}\right) = 0$$

- Note that for n=1 the e has a more negative energy than it does for n>1, ...
- …..which means that the e is more tightly bound in the smallest allowed orbit.

Bohr atomic model

- The change in energy ΔE when the electron falls from a lower level to a higher one or vice versa is

$$\Delta E = \text{energy of final state} - \text{energy of initial state}$$

- Electrons could jump from one orbit to another only by *emitting or absorbing energy in fixed quanta*.
- eg, if an e jumps one orbit closer to the nucleus, it must emit energy equal to the difference of the energies of the two orbits.

Bohr atomic model

- Conversely, when the electron jumps to a larger orbit, it must absorb a quantum of light equal in energy to the difference in orbits.

- If there is a -ve sign for the change in energy indicates that the atom has lost energy and is now in a more stable state.

Bohr atomic model

- The wavelength of the emitted photon can be calculated from the equation

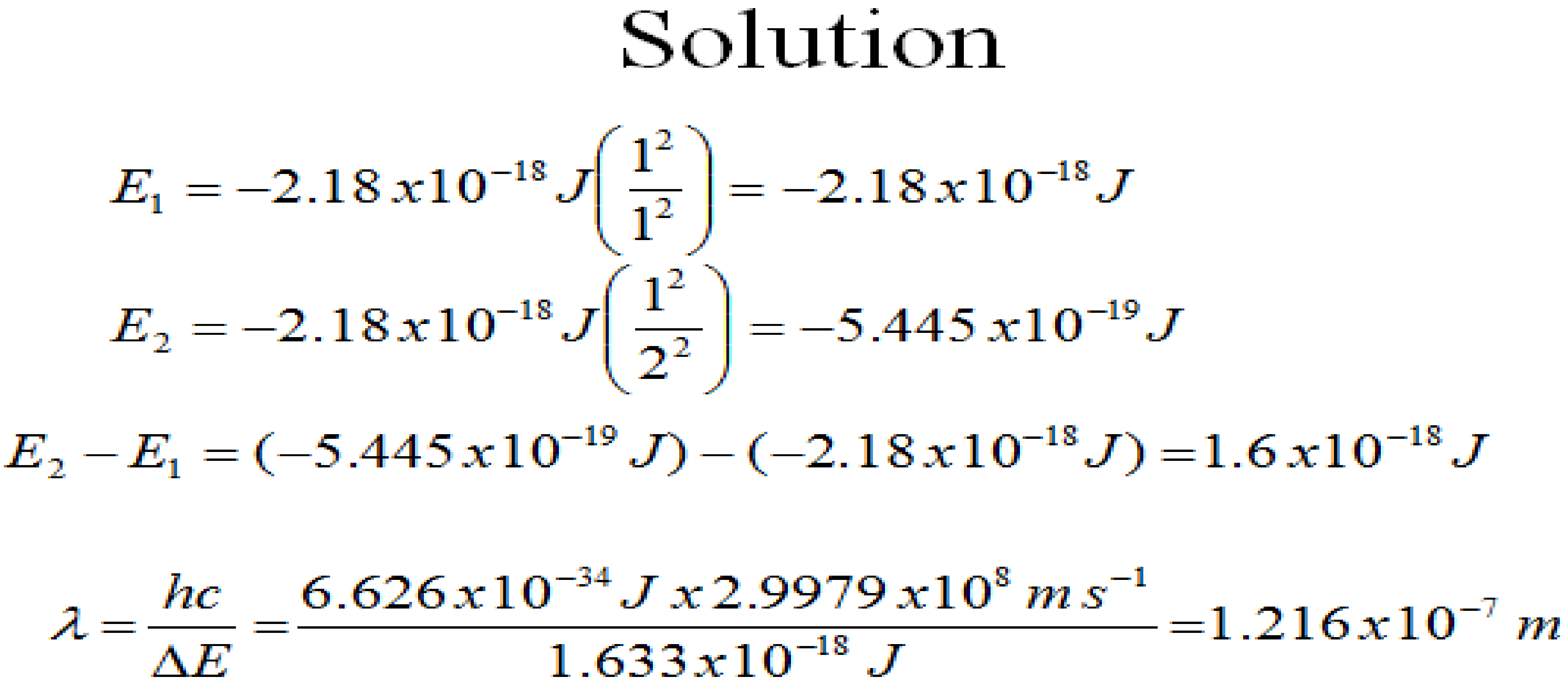
$$\Delta E = h\left(\frac{c}{\lambda}\right) \quad \text{or} \quad \lambda = \frac{hc}{\Delta E}$$

- where ΔE represents the change in energy of the atom, which equals the energy of the emitted photon.

Example:

- 1. Calculate the energy required to excite the hydrogen atom from level n = 1 to level n = 2. Also calculate the wavelength of light that must be absorbed by a hydrogen atom in its ground state to reach this excited state.

Solution



Solution

$$E_1 = -2.18\,x10^{-18}\,J\left(\frac{1^2}{1^2}\right) = -2.18\,x10^{-18}\,J$$

$$E_2 = -2.18\,x10^{-18}\,J\left(\frac{1^2}{2^2}\right) = -5.445\,x10^{-19}\,J$$

$$E_2 - E_1 = (-5.445\,x10^{-19}\,J) - (-2.18\,x10^{-18}\,J) = 1.6\,x10^{-18}\,J$$

$$\lambda = \frac{hc}{\Delta E} = \frac{6.626\,x10^{-34}\,J\,x\,2.9979\,x10^{8}\,m\,s^{-1}}{1.633\,x10^{-18}\,J} = 1.216\,x10^{-7}\,m$$

Determination of wavelength associated with e transition

- 2nd method
- Since energy associated with a particular orbit (energy level) is known i.e

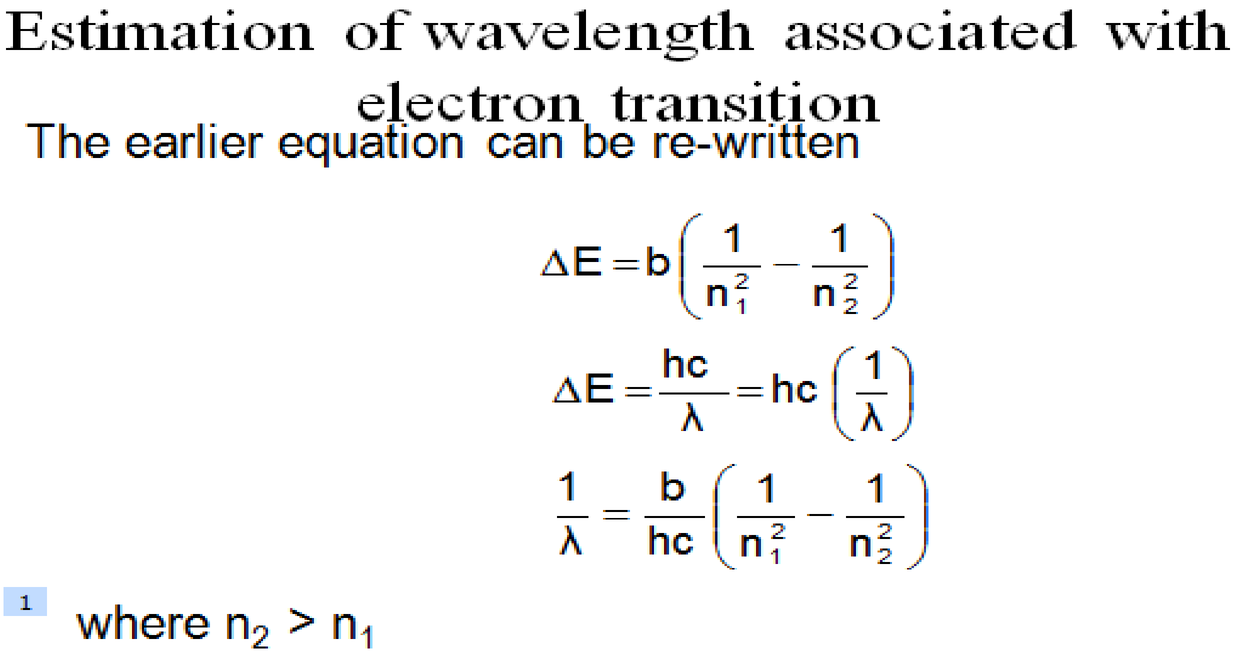
$$E = -\frac{b}{n^2}$$

$$\Delta E = E_{n_2} - E_{n_1}$$

$$\Delta E = -\left(\frac{b}{n_2^2}\right) - \left(-\frac{b}{n_1^2}\right)$$

$$\Delta E = b\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Bohr model



Estimation of wavelength associated with electron transition

The earlier equation can be re-written

$$\Delta E = b\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$\Delta E = \frac{hc}{\lambda} = hc\left(\frac{1}{\lambda}\right)$$

$$\frac{1}{\lambda} = \frac{b}{hc}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

1

where $n_2 > n_1$

- b/hc has a value of 109, 730 cm^{-1} differs only by 0.05 % from experimentally determined value of R_H

Bohr Theories

- The eq derived from Bohr’s theory matches the Rydberg equation obtained from atomic spectrum of hydrogen
- The Rydberg equation can be used to calculate all the wavelengths of the spectral lines of hydrogen

$$\frac{1}{\lambda} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

- where R_H is the Rydberg constant = 109,678 cm^{-1}

Bohr model

- We can draw the following points so far:
  - Energy of an electron in any particular orbit can be calculated.
  - The energy of the e depends on the orbit it occupies.
  - The smaller the radius of the orbit, the lower the energy of the electron in the orbit stable is the atom.
  - Allowed values of n are whole numbers n = 1, 2, 3,4 …

Bohr model

- According to Bohr model, the e does not fall into the nucleus because it cannot occupy an orbit with a radius smaller than radius of the first orbit or energy lower than the energy of the first orbit.
- When the e is in the lowest orbital, the H atom is said to b in its *ground state* & when in a higher level it is in an *excited stated*.
-

Drawbacks of Bohr’s theory

- **Bohr’s theory - great accomplishment but was flawed.**

- Biggest contribution in his model was to **introduce quantum principles** to classical physics, but his model had a few limitations/drawbacks.

1. The model could make accurate predictions for the smaller sized atoms like Hydrogen, but it failed to make predictions for larger atoms.

- As more evidence is gathered about the e, Bohr’s idea of an electron in an “orbit” is discredited

Drawbacks of Bohr’s theory

2. According to Bohr, the radiation results when an electron jumps from one energy orbit to another energy orbit, but how this radiation occurs is not explained by Bohr.

3. Mixture of Sciences…The Bohr model was a **mixture of quantum & classical physics.**

- This is an issue because it was thought that quantum physics was **completely irrelevant** and different to classical physics.

Drawbacks of Bohr’s theory

4. Bohr assumes that an e in an atom is located at a definite distance from the nucleus & is revolving round it with definite velocity.

- i.e. it is associated with a fixed value of momentum.
- This is against the Heisenberg's Uncertainty Principle according to which it is *impossible to determine simultaneously with certainty the position & the momentum of a particle.*

EXAMPLE!

Calculate the energy required to excite the hydrogen electron from level n = 1 to level n = 2. Also calculate the wavelength of light that must be absorbed by a hydrogen atom in its ground state to reach this excited state.

Using Equation,

$$E = -2.178 \times 10^{-18} J (z^2 / n^2)$$

with Z = 1 we have

$E_1 = -2.178 \times 10^{-18} J(1^2/1^2) = -2.178 \times 10^{-18} J$

$E_2 = -2.178 \times 10^{-18} J(1^2/2^2) = -5.445 \times 10^{-19} J$

$\Delta E = E_2 - E_1 = (-5.445 \times 10^{-19} J) - (-2.178 \times 10^{-18} J)$

$= 1.633 \times 10^{-18} J$

The positive value for ∆E indicates that the system has gained energy. The wavelength of light that must be absorbed to produce this change is

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34}\ \text{J.s})(2.9979 \times 10^{8}\ \text{m/s})}{1.633 \times 10^{-18}\ \text{J}}$$

$$= 1.216 \times 10^{-7}\ \text{m}$$

EXAMPLE!

Calculate the energy required to remove the electron from a hydrogen atom in its ground state.

- ✓ **Solution**: Removing the electron from a hydrogen atom in its ground state corresponds to taking the electron from $n_{initial} = 1$ to $n_{final} = \propto$. Thus,

$$\Delta E = -2.178 \times 10^{-18}\ \text{J} \left[\frac{1}{n^2_{final}} - \frac{1}{n^2_{initial}} \right]$$

$$= -2.178 \times 10^{-18}\ \text{J} \left[\frac{1}{\propto} - \frac{1}{1^2} \right]$$

The energy required to remove the electron from a hydrogen atom in its ground state is 2.178 x 10^{-18} J.

EXAMPLE!

What color of light is emitted when an excited electron in the hydrogen atom falls from:

a) n = 5 to n = 2

b) n = 4 to n = 2

c) n = 3 to n = 2

blue, λ = 434 nm

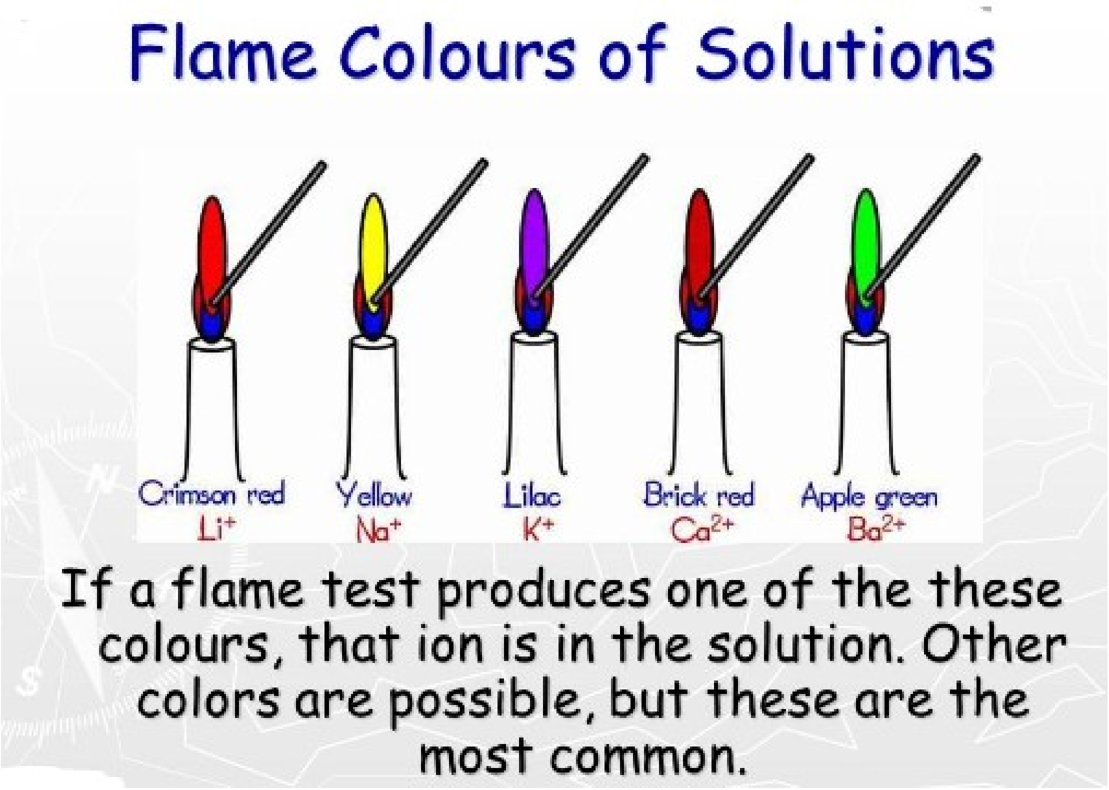
green, λ = 486 nm

orange/red, λ = 657 nm

Which transition results in the longest wavelength of light?

Atomic Spectra & the Bohr Model

- Let’s first consider the following:
- You are aware of the flame tests for identifying cations in **qualitative analysis.**
- Na impart a bright yellow colour to the flame, Cu gives a green flame.
- If we pass such a light through a **prism** it gets **separated into a set of lines.**
- This is called as a **line spectrum.**



If a flame test produces one of the these colours, that ion is in the solution. Other colors are possible, but these are the most common.

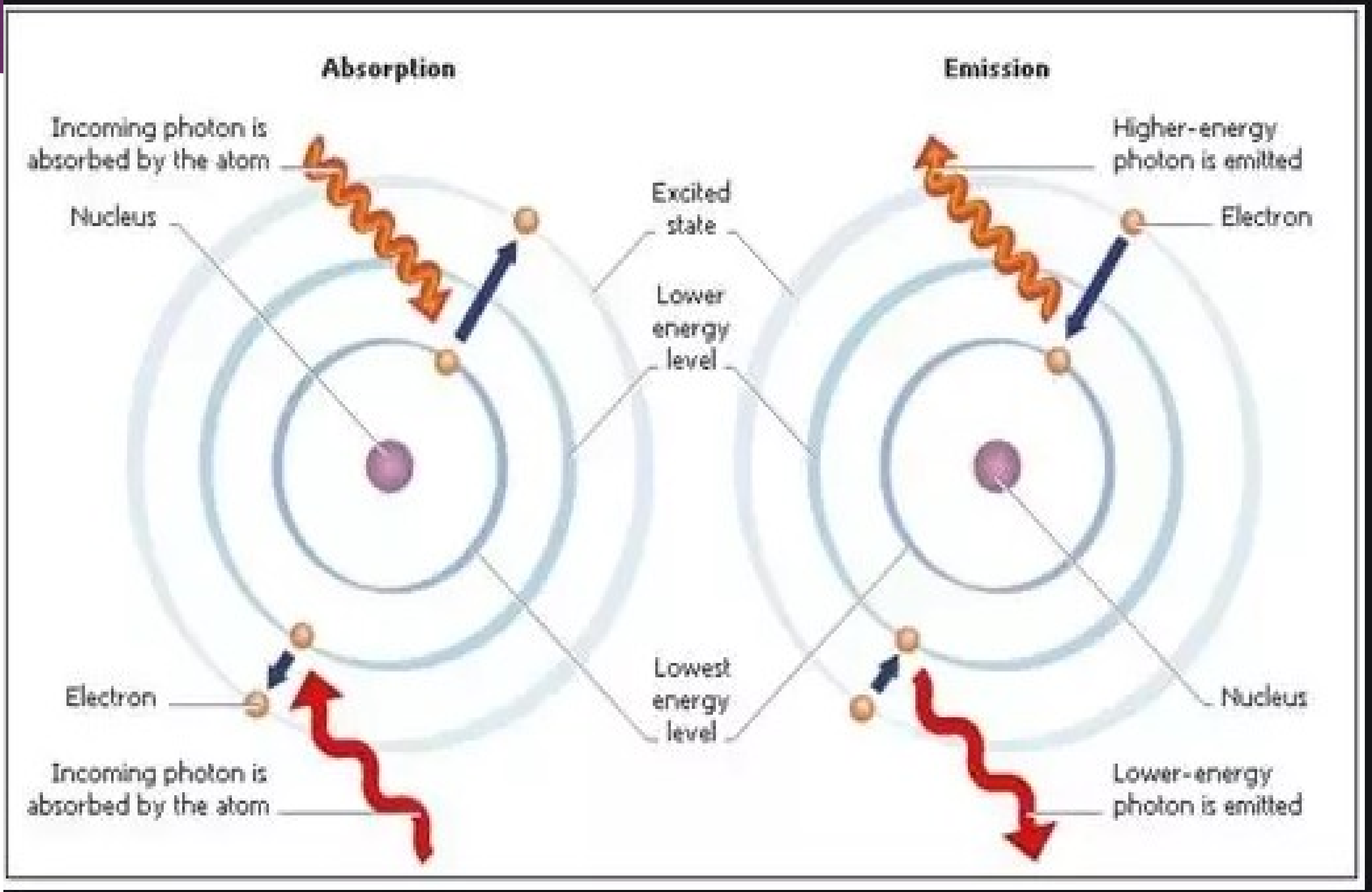
Atomic Spectra & the Bohr Model

- **Each Element Has Its Own Spectrum!!!**
- By passing an electric current or an electric spark through certain types of matter, it's possible to make that matter glow.
- Ne lights are one common example of this phenomenon.
- When an electric current travels through Ne gas, the Ne glows bright orange.
- Electricity (energy) causes *every* element

Atomic Spectra & the Bohr Model

- Another important experiment was the study of the emission of light by **excited H atoms.**

- Greatly helped in the study of atomic structure.

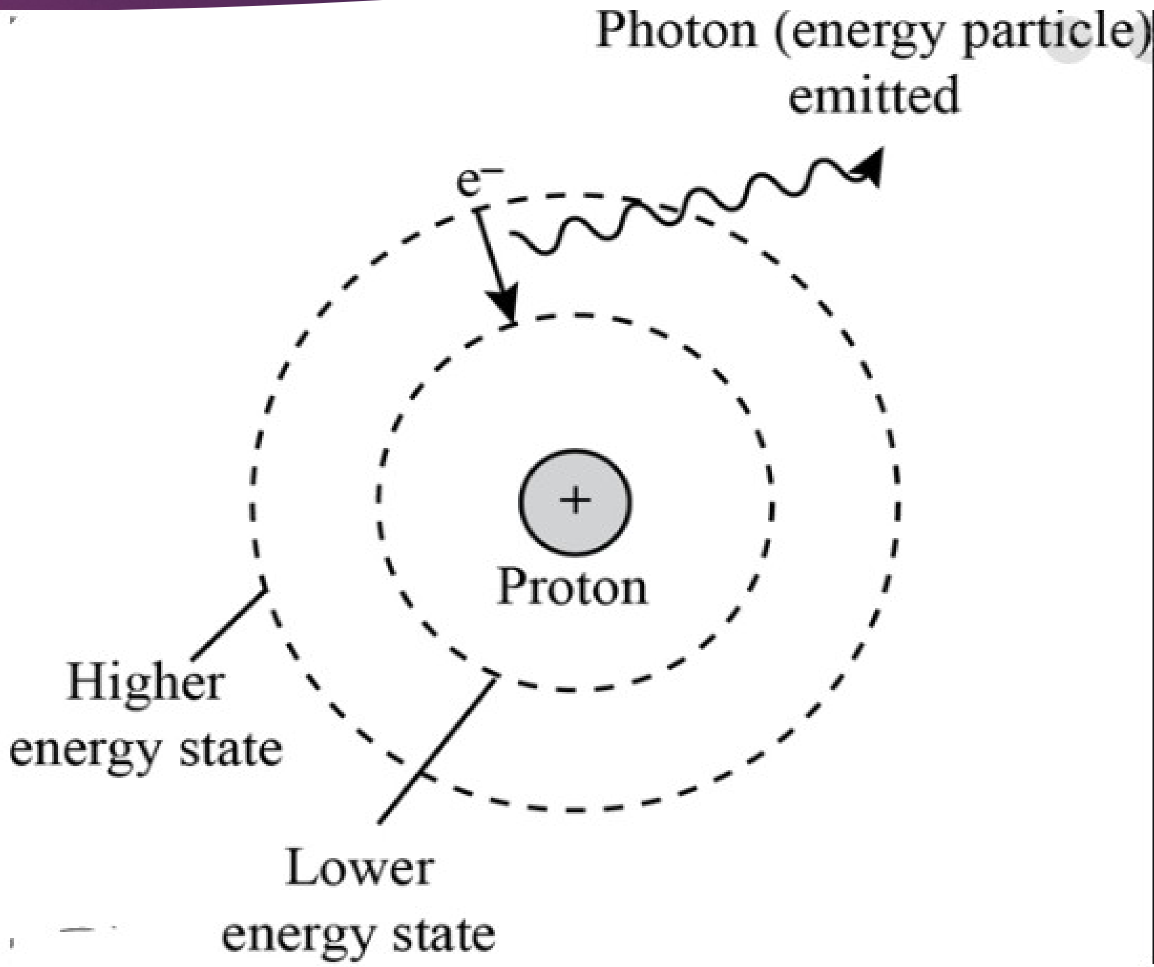


Atomic Spectra & the Bohr Model

- An atom emits a photon when it "jumps" from a higher state (state with higher energy) to lower.

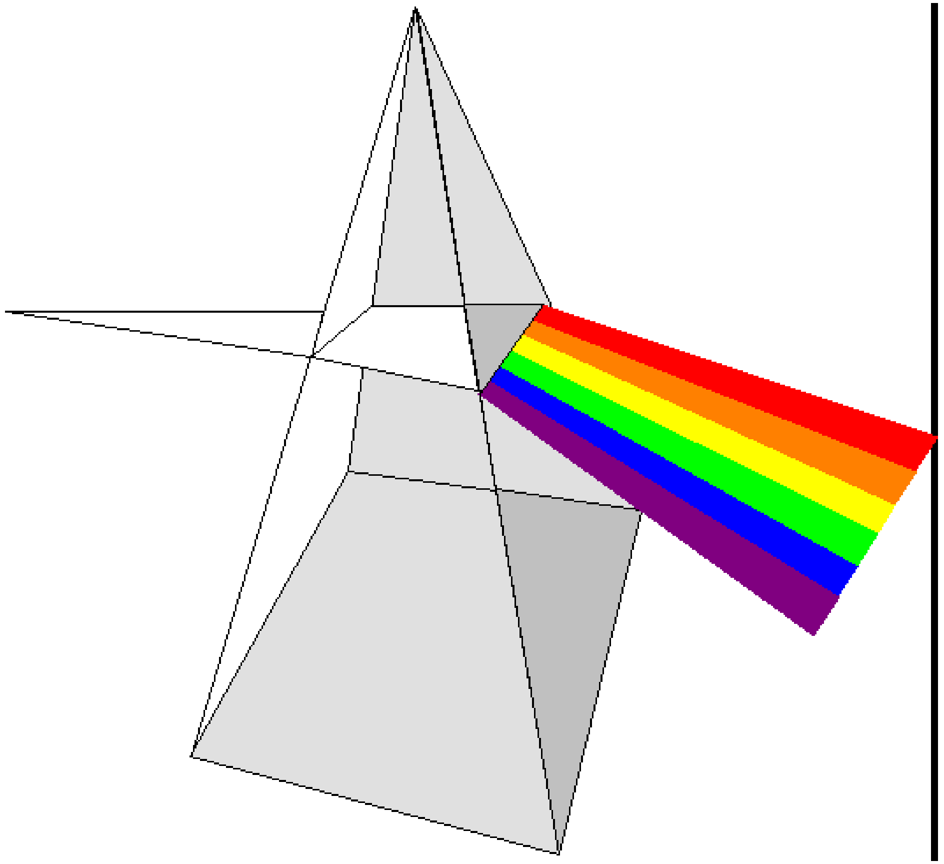
- As the energy of a state is discrete, so are the energies associated with these jumps (or transitions).

- Specific wavelength are emitted.!



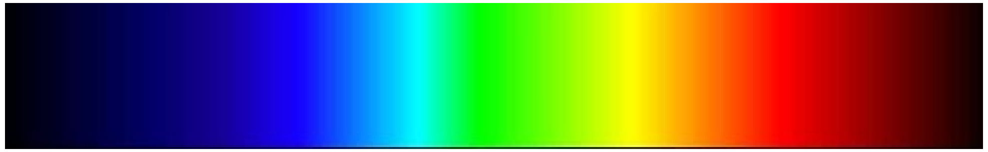
continuous spectrum

- To understand the significance of the H emission spectrum, we must first describe the **continuous spectrum….**
- This results when white light is passed through a **prism.**
- When we pass a beam of sunlight through a) we get a range of colours.
- The first **continuous spectrum** starts with a deep indigo blue & ends with red.



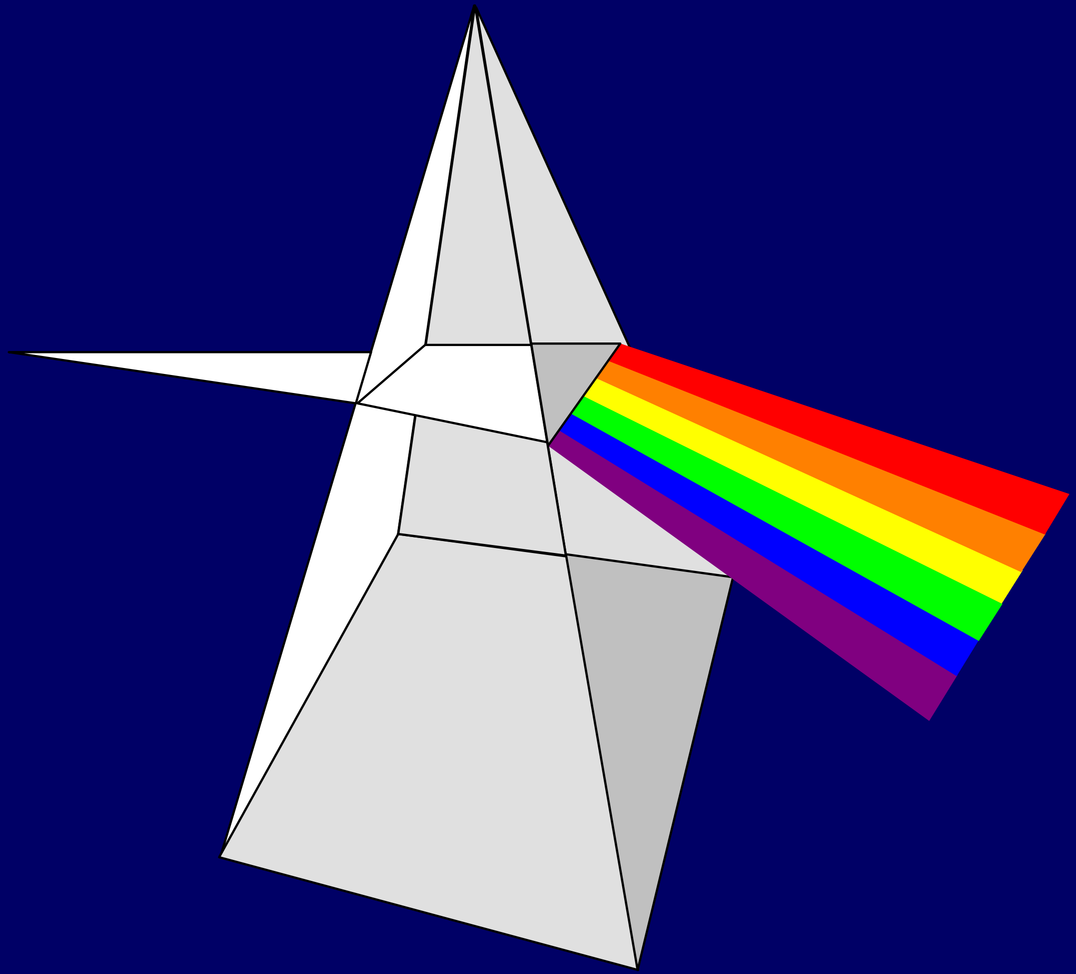
Continuous spectrum

- Notice how the colors in this spectrum change smoothly all the way from indigo to red.
- There are no gaps, or missing colors.
- Colors in the spectrum change smoothly without any gaps or holes, which makes the spectrum continuous.



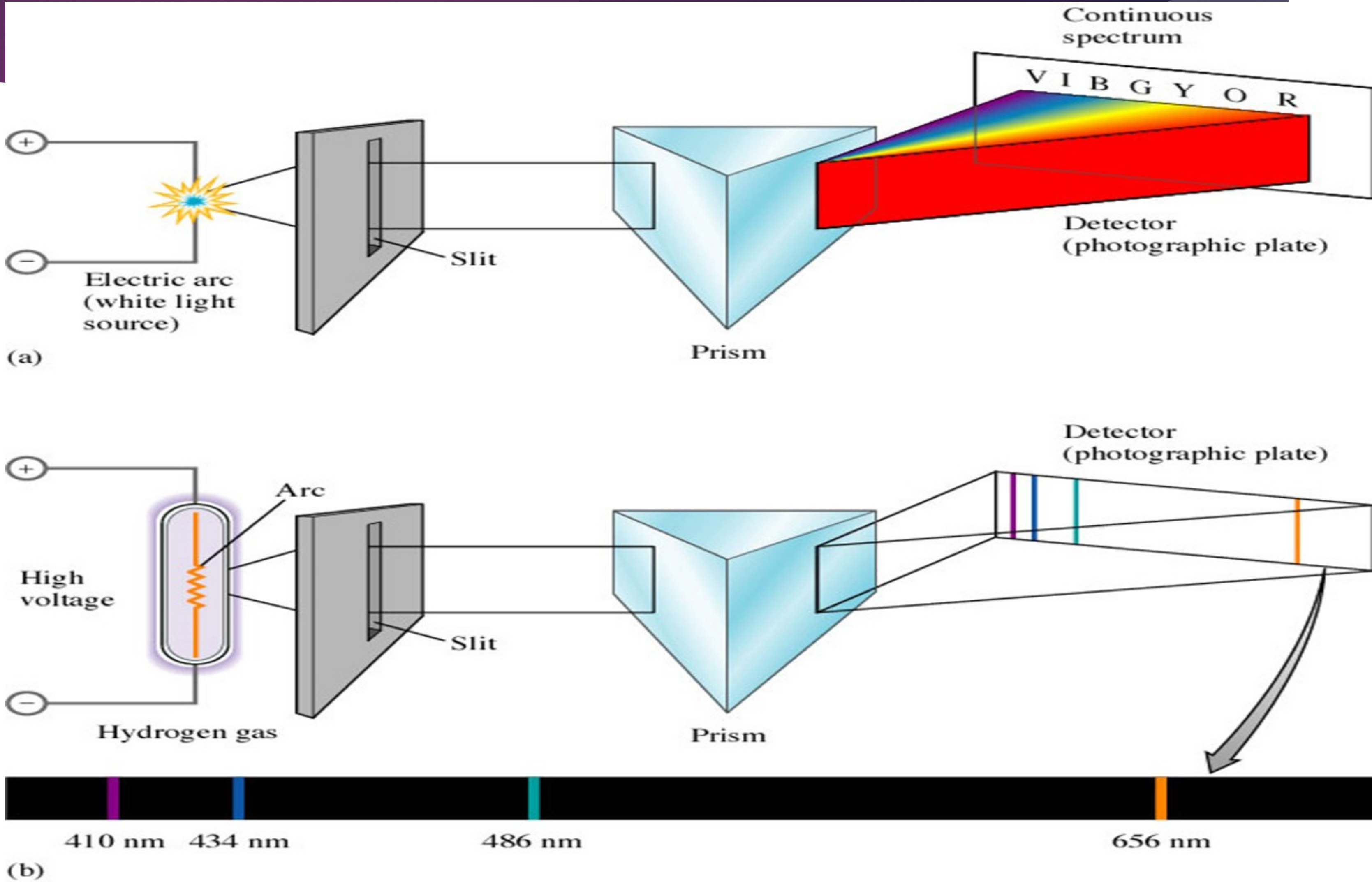
Prism

- White light is made up of all the colors of the visible spectrum.
- Passing it through a prism separates it.

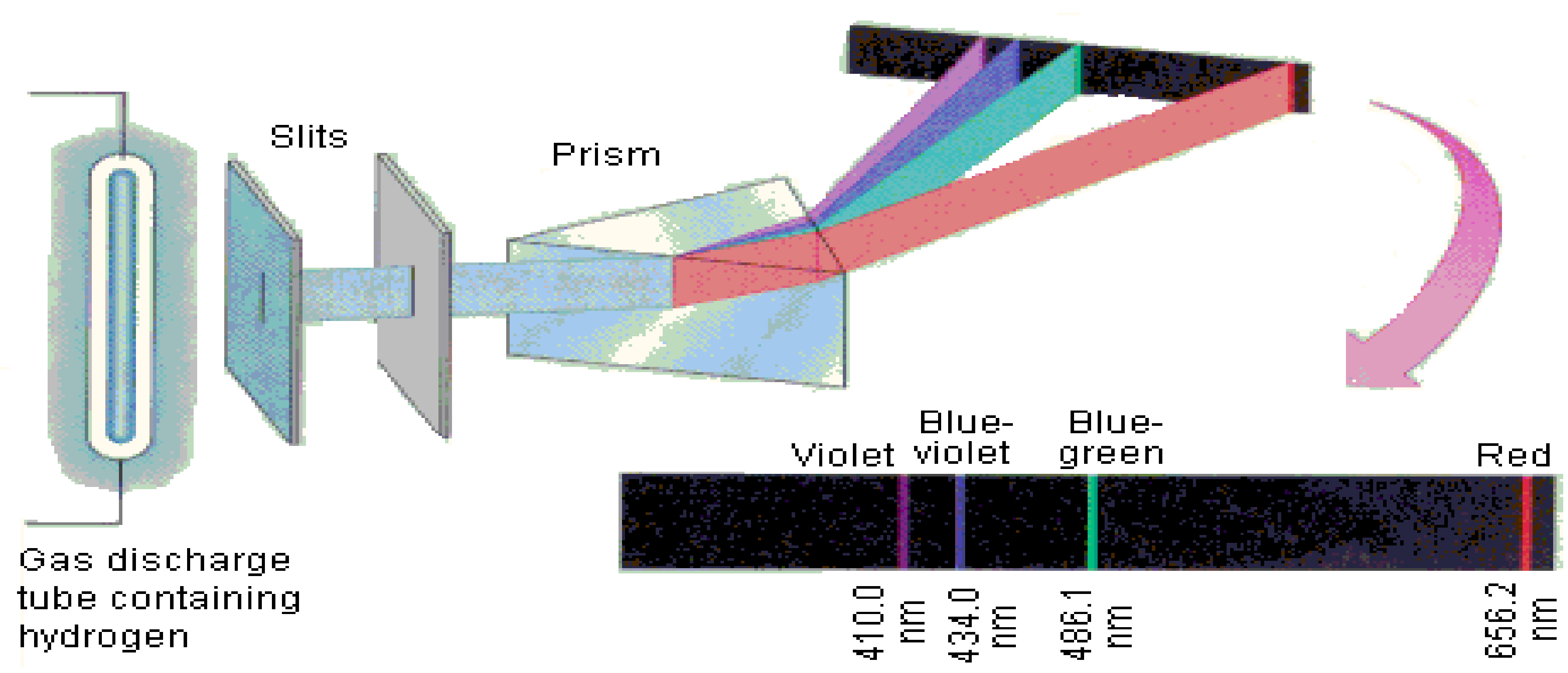


Atomic spectra of hydrogen

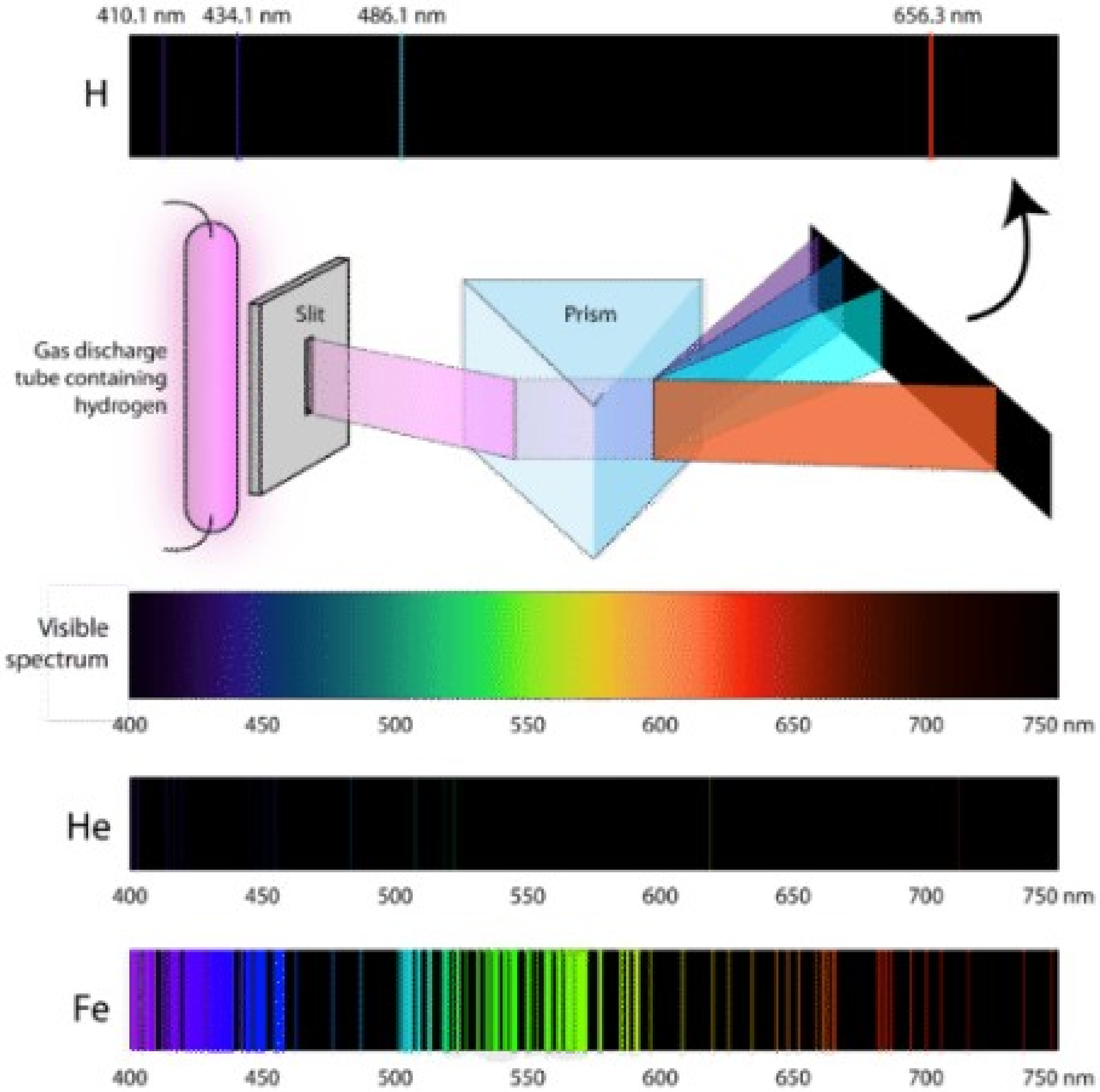
- When an **electric current** is passed through a glass tube that contains hydrogen gas at low pressure the tube gives off blue light.
- When this light is passed through a prism, 4 narrow bands of bright light are observed against a black background.



Atomic spectra of hydrogen



- ➢**This is called a line emission spectrum of H atom**



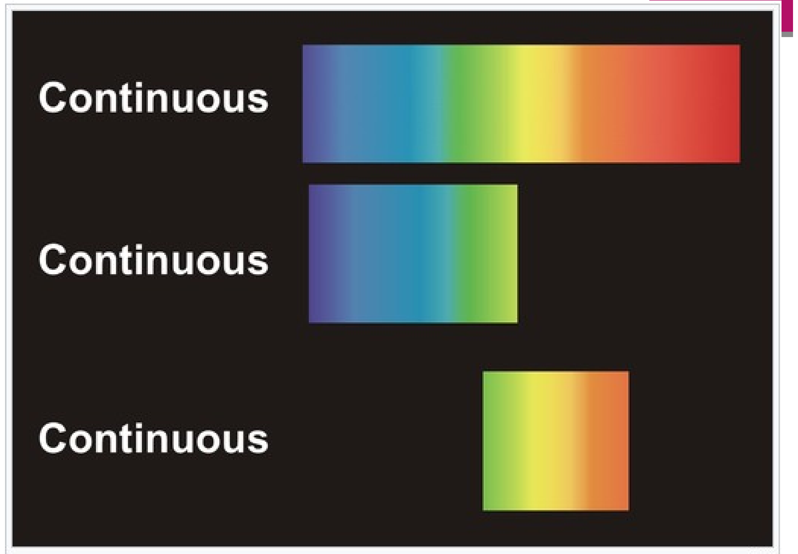
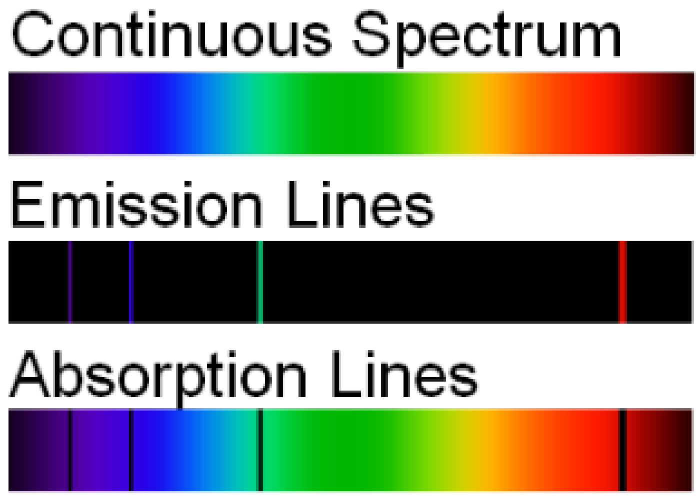
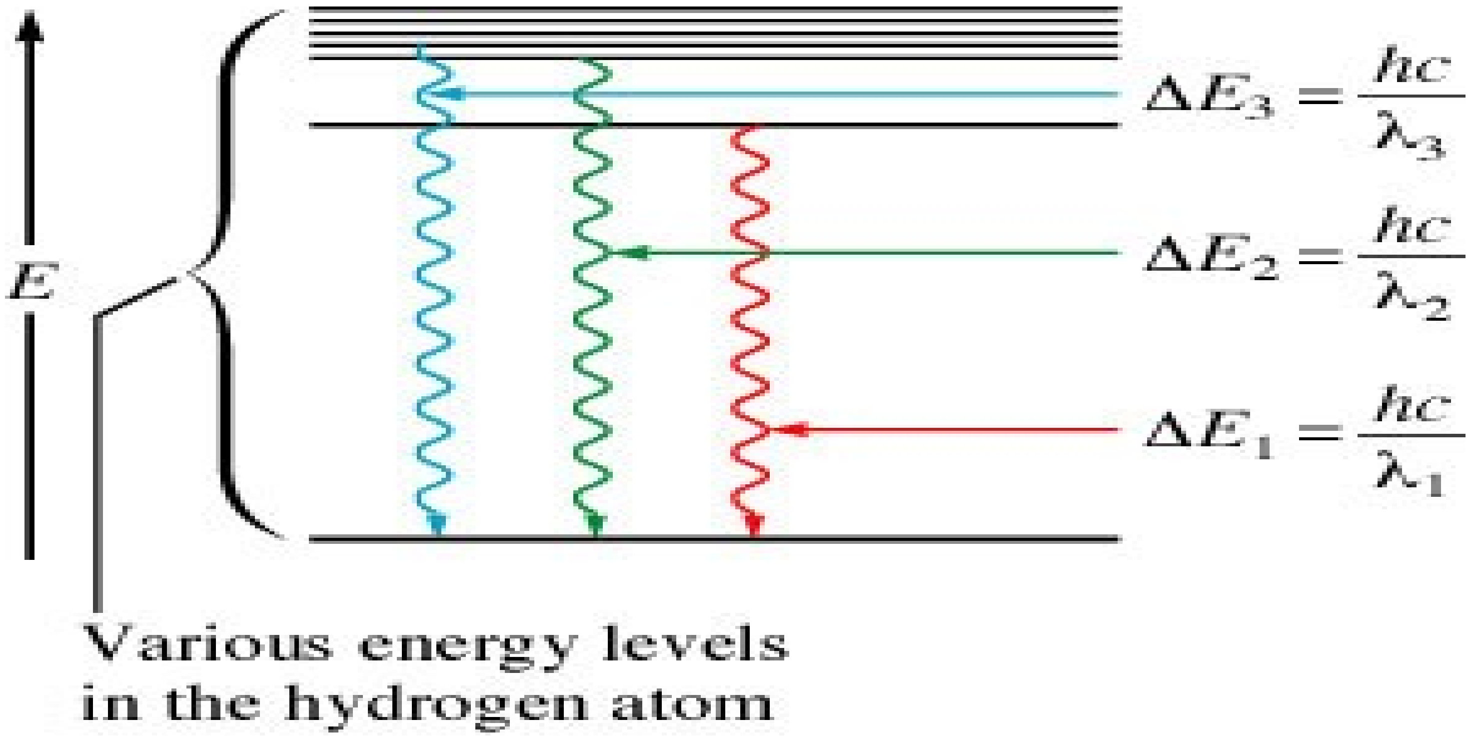


Figure 5.13: Several examples of continuous spectra in the visible range.



Significance

- Only certain energies are allowed for the electron in the hydrogen atom.
- Energy of the electron in the hydrogen atom is quantized.
- A Change between Two Discrete Energy Levels



Hydrogen (Line) spectra

- These narrow bands have the characteristic wavelengths and colors shown below.

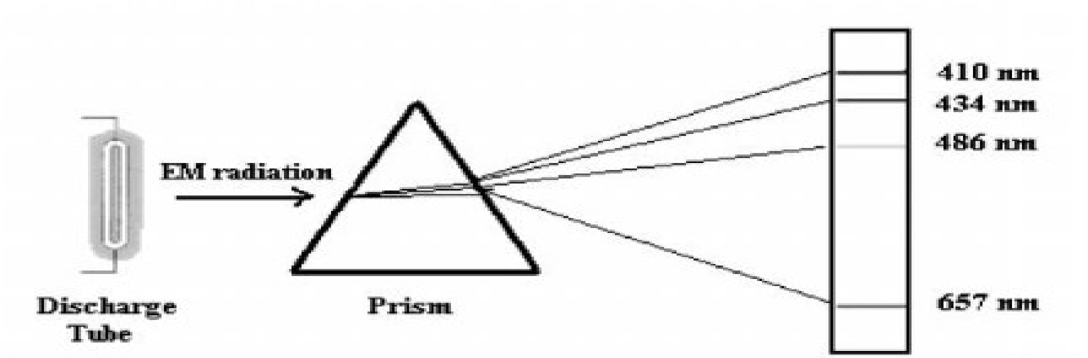


Fig. 3.9: *A schematic diagram showing line spectrum of hydrogen in the visible range*

Johann Balmer (1825-1898)

Hydrogen (Line) spectra

- These observed spectral lines are due to the electron making transitions between two energy levels in the atom
  - ✓ If the energy of the electron is increasing, this is from absorption of the light energy.
  - ✓ If the light is being emitted, this is from the energy of the electron decreasing.

- The emission spectrum of atomic hydrogen has been divided into a number of spectral series, with wavelengths given by the **Rydberg formula.**

Hydrogen (line)spectra

- These spectral emission lines (studied by different scientists) could be expressed in the form of a general formula as:

$$\bar{\nu} = \frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{ cm}^{-1} \text{ ; } R_H = 109677 \text{ cm}^{-1}$$

  - *Where n_1 & n_2 are positive integers ($n_1 < n_2$) (known as the principle quantum number) lamda is wavelength of light emitted and R_H is called Rydberg's constant.*

- This Formula is known as the ***Rydberg equation***.
- The classification of the series by the Rydberg formula was important in the development of **quantum mechanics**

Hydrogen (Line) spectra

- The specific wavelengths of light that are either absorbed or emitted from a sample of H atoms, are associated with electronic transitions.
- This means that there are discrete energy levels that the electron is moving between.

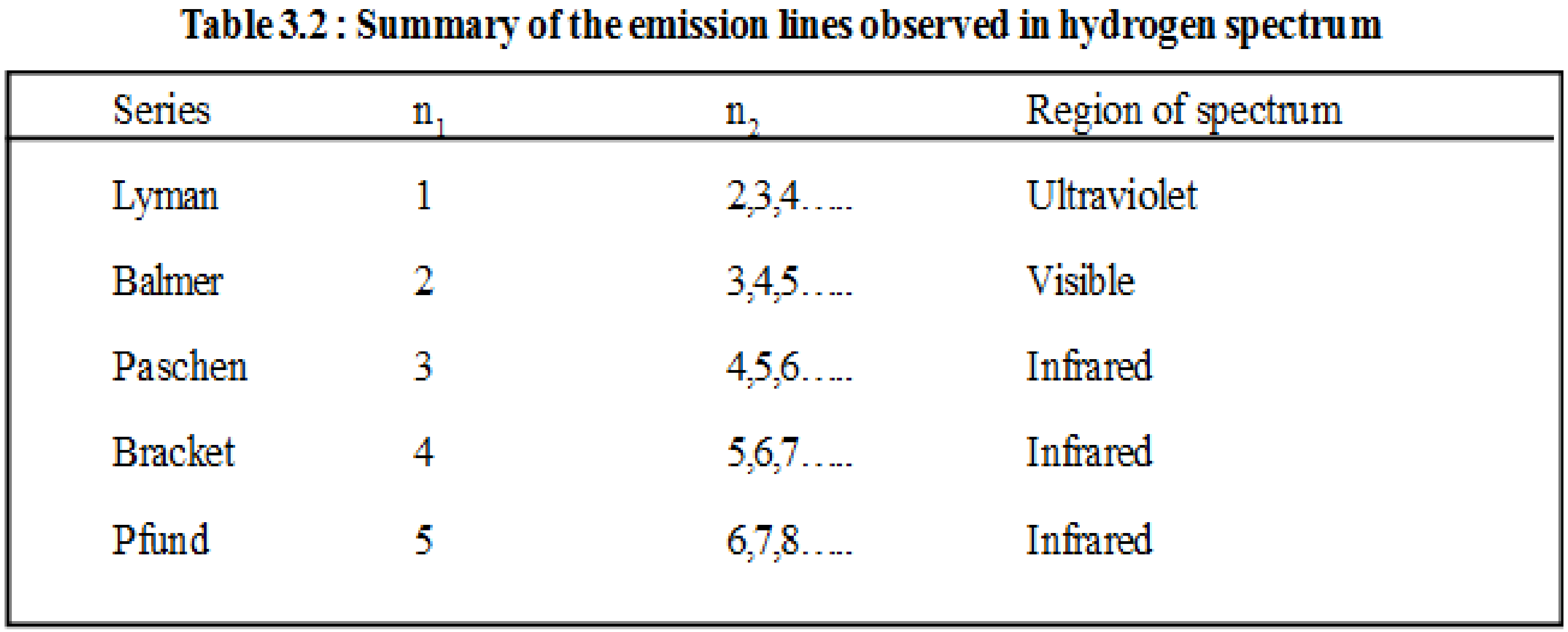


Table 3.2 : Summary of the emission lines observed in hydrogen spectrum

Series	n_1	n_2	Region of spectrum
Lyman	1	2,3,4…..	Ultraviolet
Balmer	2	3,4,5…..	Visible
Paschen	3	4,5,6…..	Infrared
Bracket	4	5,6,7…..	Infrared
Pfund	5	6,7,8…..	Infrared

CONCEPT CHECK!

- ✓ Why is it significant that the color emitted from the hydrogen emission spectrum is not **white**?

- ✓ How does the emission spectrum support the idea of quantized energy levels?

EXAMPLE!

Calculate the wavelength of the Balmer line with an electronic transition corresponding to $n_2 = 3$

Solution: According to Balmer series $\overline{\nu} = R_H \left(\frac{1}{2^2} - \frac{1}{n_2^2} \right)$

where $R_H = 109{,}677\ \text{cm}^{-1}$

$$\text{For } n_2 = 3\ ;\ \overline{\nu} = 109{,}677 \left(\frac{1}{2^2} - \frac{1}{3^2} \right) = 109{,}677 \left(\frac{5}{36} \right)$$

$$\text{Since,} \quad \lambda = \frac{1}{\nu}\ ;\ \lambda = \frac{36}{109{,}677 \times 5}$$

$$= 6.56 \text{ x } 10^{-5}\ \text{cm}$$

$$= 656\ \text{nm}$$