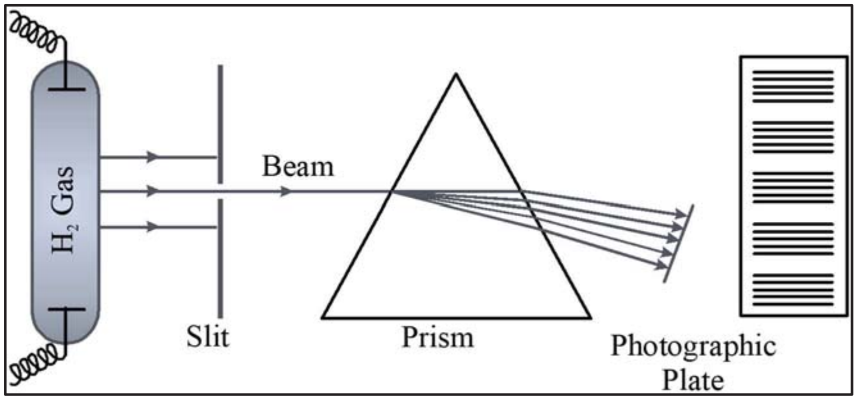
LINE SPECTRUM OF HYDROGEN ATOM

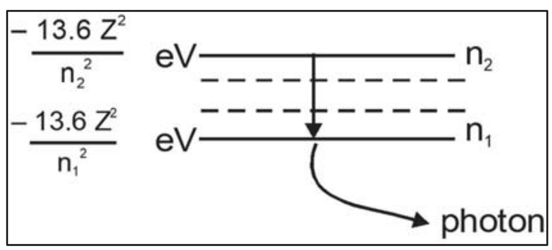
Emission Spectrum of Hydrogen



When hydrogen gas is introduced into a discharge tube at low pressure, and the light emitted during the passage of an electric discharge is observed through a spectroscope, the resulting spectrum is referred to as the emission spectrum of hydrogen.

Line Spectrum of Hydrogen

The observation of the hydrogen line spectrum occurs as a result of the excitation or de-excitation of an electron moving from one stationary orbit to another. Consider an electron transitioning from n_2 to n_1 (where $n_2 > n_1$) in a hydrogen-like sample.



Energy of emitted photon = $(\Delta E)_{n2n1} = \frac{-13.6Z^2}{n_2^2} - (\frac{-13.6Z^2}{n_1^2})$

$= 13.6Z^2 (\frac{1}{n_1^2} - \frac{1}{n_2^2})$

$= (\Delta E)_n 2n1$ =Wavelength of emitted photon

$$\lambda = \frac{hc}{(\Delta E)_{n_2 \to n_1}}$$

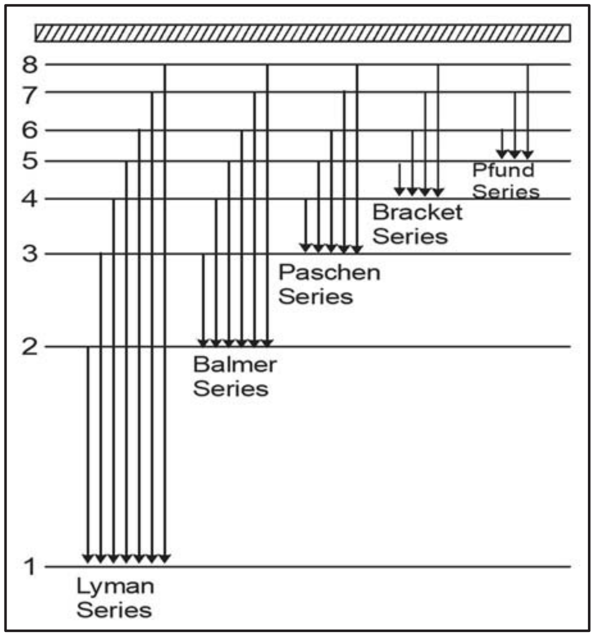
$$\lambda = \frac{hc}{13.6Z^2(\frac{1}{n_1^2} - \frac{1}{n_2^2})}$$

$$\frac{1}{\lambda} = \frac{(13.6)z^2}{hc}(\frac{1}{n_1^2} - \frac{1}{n_2^2})$$

Wave number, $\frac{1}{\lambda} = \overline{v} = R^2 (\frac{1}{n_1^2} - \frac{1}{n_2^2})$

R = Rydberg constant = $1.09678 \times 10^7 m^{-1}$;

R $1.1 \times 10^7\ m^{-1}$; R = $\frac{13.6eV}{hc}$; R ch = 13.6 eV



Ex. Calculate the wavelength of a photon emitted when an electron in H- atom maker a transition from n = 2 to n = 1

Sol. $\frac{1}{\lambda} = RZ^2\left[\frac{1}{N_1^2} - \frac{1}{N_2^2}\right]$

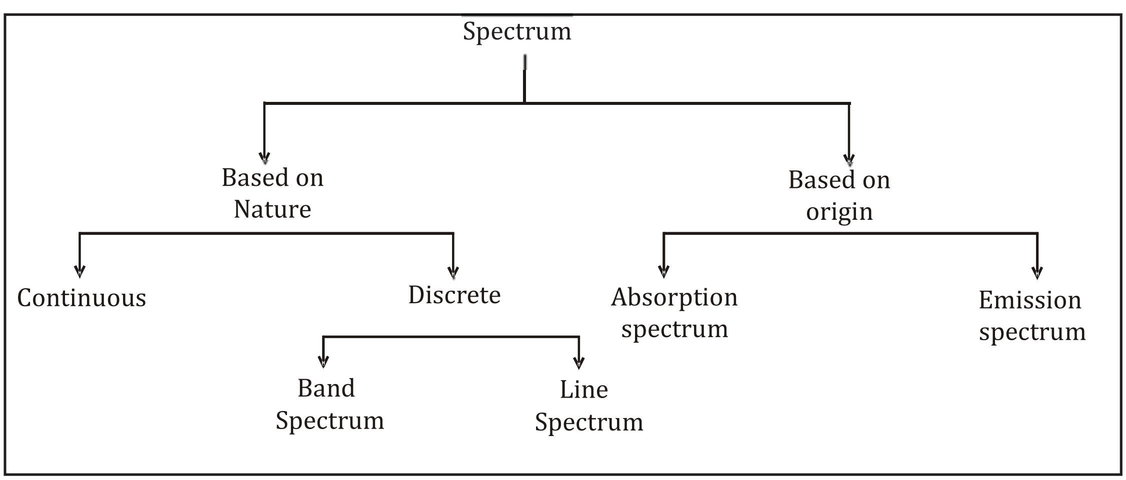
$\therefore \quad \frac{1}{\lambda} = R(1)^2\left[\frac{1}{1^2} - \frac{1}{2^2}\right]$

$\therefore \quad \frac{1}{\lambda} = \frac{3R}{4}$ or $\lambda = \frac{4}{3R}$

Hydrogen Spectrum

Study of Emission and Absorption Spectra

A device employed to disperse radiation into distinct wavelengths or frequencies is termed a spectroscope or spectrograph. The recorded photograph or pattern of the emerging radiation on the film is referred to as a spectrogram or simply a spectrum of the given radiation. The scientific field focused on the study of spectra is known as spectroscopy.



Rydberg Constant

In the field of spectroscopy within the realm of physics, the Rydberg constant holds significance as a physical constant that establishes a connection with atomic spectra. Designated as R_∞ when applied to heavy atoms and as R_H specifically for hydrogen, the Rydberg constant initially emerged as a fitting parameter in the Rydberg formula. Initially introduced as a means to characterize spectral lines, the Rydberg constant gained prominence as Niels Bohr later undertook the calculation of this constant using fundamental constants. This transition from a fitting parameter to a value derived from foundational principles underscored its importance in providing a deeper understanding of atomic behavior and contributed to the refinement of theoretical models in the study of atomic spectra.

Equation for the Rydberg Constant

Niels Bohr demonstrated the Rydberg Constant equation, employing fundamental constants to elucidate relationships within the framework of the Bohr model. This constant plays a pivotal role in the formulation of wavenumbers for lines observed in atomic spectra. Its derivation is intricately linked to key physical parameters such as the rest mass and charge of the electron, the speed of light, and Planck's constant. By incorporating these fundamental constants, the Rydberg Constant equation serves as a fundamental tool for understanding and predicting the characteristics of atomic spectral lines, contributing significantly to the advancement of atomic physics.

Modification of Rydberg Equation

Formula: $$\bar{V} = \frac{2\pi m e^4 K^2 Z^2}{Ch^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

This equation incorporates the concept of reduced mass (μ) when describing the motion of an electron and a nucleus around their common center of mass. The introduction of reduced mass is particularly relevant in scenarios where the mass of the electron is significantly smaller than that of the nucleus.

The reduced mass (μ) is defined as $\mu = \frac{m_e . m_n}{m_n + m_e}$,

where m_e is the mass of the electron and m_n is the mass of the nucleus. In situations where m_n is substantially greater than m_e ($m_n \gg m_e$), the reduced mass (μ) approximates the mass of the electron ($\mu = m_e$).

This approximation is justified by the assumption that the mass of the nucleus (m_n) is significantly larger than the mass of the electron (m_e), allowing the term $m_n + m_e$ to be effectively replaced by m_n. Consequently, $\mu = m_e$, and the reduced mass effect is generally neglected in routine calculations.

However, it becomes pertinent to consider the reduced mass effect in specific scenarios:

(a) When the mass of the nucleus and an extranuclear particle are comparable. This situation may arise in hypothetical atoms where such parity exists.

(b) When comparing parameters of isotopes. In isotopes of an element, the atomic number (Z-value) remains constant, and any differences arise solely from variations in their nuclear masses. In such cases, the reduced mass effect should be taken into account for accurate comparisons.

Limitation of Bohr's Model: Zeeman Effect, Stark Effect

Bohr Model Limitations:

The Bohr model, despite its success in explaining certain atomic phenomena, encounters several limitations in comprehensively describing the intricacies of atomic behavior. These limitations include:

(i) Zeeman Effect: The Bohr model fails to account for the Zeeman effect, where placing a spectral line source in a magnetic field result in the splitting of spectral lines into sublines.

(ii) Stark Effect: Similarly, the model does not accommodate the Stark effect, wherein the application of an electric field causes the splitting of spectral lines.

(iii) Dual Nature of Matter: The Bohr model does not address the dual nature of matter as proposed by Einstein. Matter, according to Einstein, exhibits both wave and particle nature. While the wave nature is substantiated through phenomena like interference, reflection, and refraction, the particle nature is demonstrated through observations like black body radiation and the photoelectric effect.

(iv) Heisenberg Uncertainty Principle: The Bohr model does not incorporate the Heisenberg uncertainty principle, a fundamental concept in quantum mechanics stating that it is impossible to simultaneously know the exact position and momentum of a particle.

(v) Spectra of Multielectron System: The model falls short in explaining the spectra of systems with multiple electrons, as it primarily focuses on hydrogen-like systems with a single electron.

(vi) Atomic Sphericity vs. Electron Path: The Bohr model depicts electron paths as circular and two-dimensional, while atoms are considered spherical and three-dimensional, creating a disparity in the representation of atomic structure.

Each of these limitations is addressed individually:

(i) Zeeman Effect

When a spectral line source is subjected to a magnetic field, the Bohr model does not elucidate the phenomenon where spectral lines split into sublines, known as the Zeeman effect.

(ii) Stark Effect

In situations where the splitting of spectral lines occurs in an electric field, the Bohr model does not account for this phenomenon, termed the Stark effect.

(iii) Dual Nature

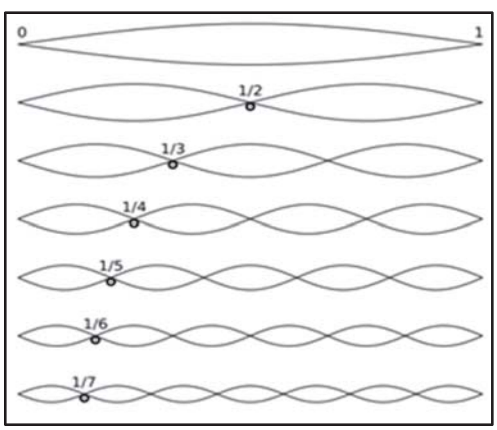
Einstein's revelation that lights exhibits both wave and particle nature is not accommodated in the Bohr model. The model does not incorporate the experimental evidence supporting both aspects of light behavior.

These limitations underscore the need for more sophisticated models, such as quantum mechanics, to comprehensively describe the behavior of subatomic particles and the intricacies of atomic systems.

Dual Nature of Matter, De-Broglie Equation

DeBroglie’s hypothesis (dual nature of matter)

De Broglie proposed that electrons, similar to light, exhibit dual nature, behaving both as material particles and waves. The notion of the dual character of matter led to a wave mechanical theory of the atom, suggesting that electrons, protons, and even atoms demonstrate wave properties when in motion.



Derivation of deBroglie's Relationship

For a photon,

$$E = \frac{hc}{\lambda} \quad \text{......(i)}$$
$$E = mc^2 \quad \text{......(ii)}$$
$$mc^2 = \frac{hc}{\lambda}$$
$$\lambda = \frac{h}{mc} = \frac{h}{p}$$

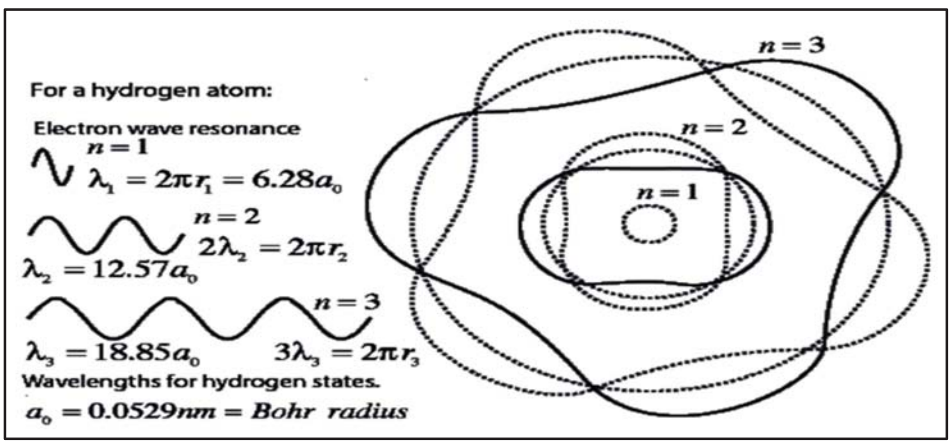
He concluded that just as electromagnetic radiation has an associated mass or momentum, similarly, every moving particle with mass 'm' and velocity 'v' is linked to waves known as matter waves or de Broglie's waves.

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

Experimentation verification of deBroglie's hypothesis: Given by Davission and Germer.

They noticed that a beam of electrons undergoes diffraction when incident on a nickel crystal, similar to X-rays. Furthermore, the wavelengths of the electrons, as determined by diffraction experiments, match the values calculated from de Broglie's relationship.

Derivation Of Bohr's Postulate of Quantisation of Angular Momentum from DeBroglie's Equations



According to de Broglie, a moving electron, associated with waves, must be entirely in phase. Consequently, only those orbits are feasible where the circumference of the orbit is an integral multiple of λ, i.e.,

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

where n is the no. of waves

$$2\pi r = \frac{nh}{mv} \quad \Rightarrow \quad mvr = \frac{nh}{2\pi}$$

From the above expression it can be commented that no of waves in a shell wave = shell no.

Calculation of deBroglie's wavelength if K.E. of the particle is E:

$$E = \frac{1}{2}mv^2$$
$$2E = mv^2$$
$$2mE = m^2v^2 = p^2$$
$$p = \sqrt{2mE}$$

$$\frac{h}{\lambda_{dB}} = \sqrt{2mE}$$

$$\lambda_{dB} = \frac{h}{\sqrt{2mE}}$$

If a charge particle at rest (having charge 'q') is accelerated by potential difference 'V' volt then

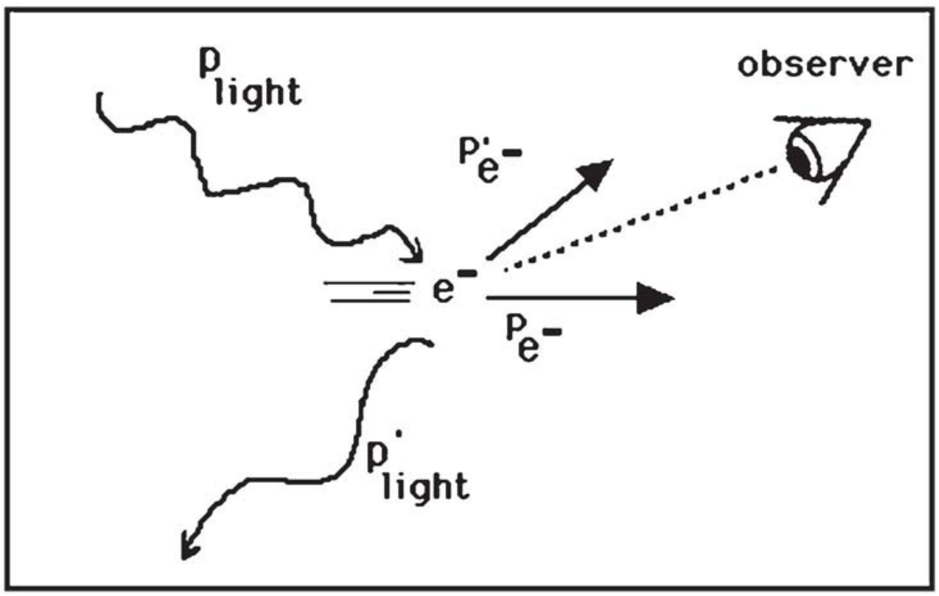
$$\lambda_{dB} = \frac{h}{\sqrt{2mqv}},$$

$$\lambda_{dB} = \sqrt{\frac{150}{V}}\,\text{Å} \quad \text{(Only for electron)}$$

Ex. Calculate λ_{dB} of electron have K.E. 3eV

Sol. $\lambda_{dB} = \sqrt{\frac{150}{3}} = \sqrt{50}$ Å

The Uncertainty Principle



The simultaneous measurement of a particle's position and momentum with arbitrarily high precision is not possible. There exists a minimum for the product of the uncertainties in these two measurements. Similarly, there is a minimum for the product of the uncertainties in energy and time.

$$\Delta x \Delta p \geq \frac{h}{4\pi}$$

$$\Delta E \Delta t \geq \frac{h}{4\pi}$$

The uncertainty principle carries implications regarding the energy needed to confine a particle within a specific volume. The energy required for particle confinement is sourced from fundamental forces. Specifically, the electromagnetic force provides the attraction essential for containing electrons within the atom, and the strong nuclear force supplies the necessary attraction for confining particles within the nucleus. However, the size of the confinement achievable by these forces is determined by Planck's constant, as outlined in the uncertainty principle. In other words, the scales of the atom and the nucleus are governed by the strengths of the nuclear and electromagnetic forces, coupled with the constraint imposed by the value of Planck's constant.