

Bohr's Condition for Stable Orbits: Only those orbits are allowed in which only integral multiple of electron's de Broglie wavelength fit

$$n\lambda = 2\pi r_n ; n = 1, 2, 3 \dots$$

$r_n$  - radius of the orbit containing  $n$  wavelengths.

$n$  - quantum number of orbit

Substituting  $\lambda$  we get

$$n \frac{h}{e} \sqrt{\frac{4\pi E_0 r_n}{m}} = 2\pi r_n$$

So the orbital radius of atom is given by

$$r_n = \frac{n^2 h^2 \epsilon_0}{4\pi m e^2} \quad n = 1, 2, 3 \dots$$

The innermost radius is called the Bohr radius as

$$a_0 = r_1 = \frac{h^2 \epsilon_0}{4\pi m e^2} = 5.292 \times 10^{-11} \text{ m}$$

All other radii can be written as  $r_n = n^2 a_0$

Energy levels & Spectra: Electron in the  $n$ th orbit has energy

$$E_n = -\frac{e^2}{8\pi\epsilon_0 r_n^2} \quad (\text{these are called energy levels})$$
$$= -\frac{me^4}{8\epsilon_0^2 h^2} \frac{1}{n^2} = \frac{E_1}{n^2}; \quad n = 1, 2, 3 \dots$$

$$E_1 = -2.18 \times 10^{-18} \text{ J} = -13.6 \text{ eV}$$

$E_n = \frac{E_1}{n^2}$  are called the energy levels of hydrogen atoms.

The negative value of  $E_1$  signifies that to make the electron escape the atom, energy has to be provided from outside. The energy that need to be provided is called the ionization energy.

Lowest energy level  $E_1$  is called ground state. The other levels are called the first excited state ( $E_2$ ), second excited state ( $E_3$ ) - etc.

\* Energy levels in atoms are discrete. When an electron in an excited state jumps to a lower state it emits energy in the form of photon. Emitted photons constitute the spectral lines.

$$\text{photon energy } h\nu = E_i - E_f \quad (\text{E}_i - \text{initial, E}_f \rightarrow \text{final})$$

$$\Rightarrow \nu = \frac{E_i - E_f}{h} = -\frac{E_1}{h} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

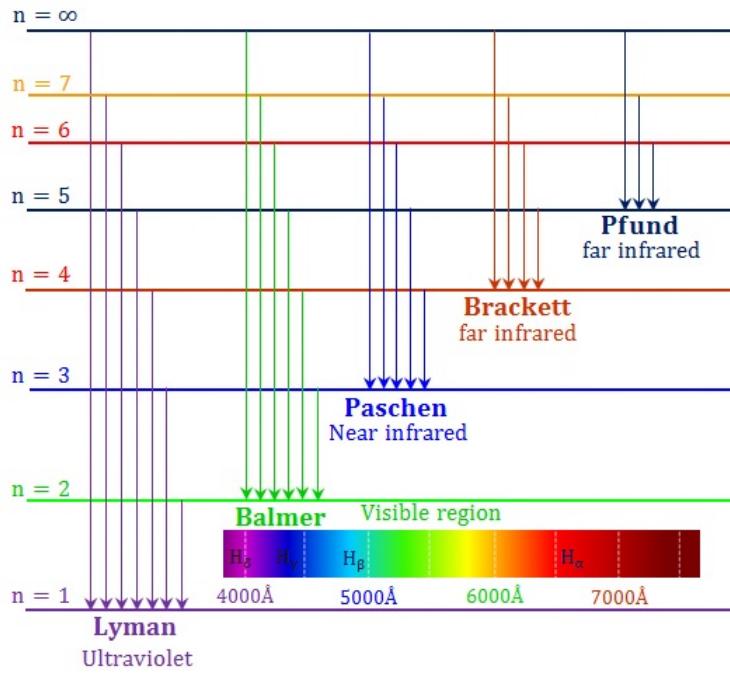
So the wavelength

$$\lambda = -\frac{E_1}{ch} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

This formula shows that the spectra must be discrete

Lyman, Balmer, Paschen etc series follow from the above formula.

# Hydrogen Spectra



For  $n = \infty$ , electron is free from atom.

Spectral lines originate in transitions between energy levels of atoms.

- \* Spectral lines of atom are evidence of quantization of atomic energy levels.
- \* The scope of Bohr's atomic theory is limited. It works for Hydrogen (and to some extent Lithium) only. A more general theory to study atomic phenomenon is required to describe spectra of other atom. This approach is called quantum mechanics.

## Quantum Mechanics $\Rightarrow$

- \* In QM all quantities related to a particle, for example its position, momentum, angular momentum, spin, energy can be established from its wave function  $\Psi$
- \*  $\Psi$  itself has no physical interpretation
- \*  $|\Psi|^2$  is interpreted as the probability density in the following way

$\int_a^b |\Psi(x,t)|^2 dx$ ; is the probability of finding the particle between  $b \leq x \leq a$  at time t

- \* In general  $\Psi$  is complex valued

$$\Psi = A + iB \quad ; \quad A \text{ & } B \text{ are real valued} \quad & i^2 = -1$$

$\Rightarrow$  Complex conjugate of  $\Psi$  is written

$$\Psi^* = A - iB$$

\* Modulus Square of  $\psi$  is always a positive real number.

$$|\psi|^2 = \psi^* \psi \quad (\text{Probability density})$$

\* Normalization Condition: As  $|\psi(x,t)|^2$  is the probability density of finding the particle,

$$\int |\psi(x,t)|^2 dx = 1 \quad \left\{ \begin{array}{l} \text{For } \psi \equiv \psi(x, y, z, t) \\ \int |\psi(x,y,z,t)|^2 dv = 1 \\ dv = dx dy dz \end{array} \right.$$

Since the particle exists somewhere in space. This is called the normalization condition.

For  $\int |\psi|^2 dx = c$  the normalized wave function is  $\psi' = \psi/\sqrt{c}$ .

\* Schrödinger Wave Equation: It gives the space & time evolution of  $\psi(x,t)$

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V(x) \psi \quad \text{Here } V(x) \text{ is potential.}$$

This is a fundamental principle of Nature. It can not be derived.

\* Expectation Value: For a particle with wavefunction if the expectation value of position  $x$  is

$$\langle x \rangle = \int_{-\infty}^{+\infty} x | \psi(x, t) |^2 dx$$

Meaning of expectation value:

\* It DOES NOT mean that if position is measured over and over again the average result will be  $\langle x \rangle$

\* Rather, what it means is the following: Suppose you have a very large number of particles all with the same wave function if then the average value of the position measurement of all the particles is  $\langle x \rangle$

We have defined  $\langle x \rangle$  assuming that it is normalized, i.e.,  $\int_{-\infty}^{+\infty} |\psi|^2 dx = 1$   
If that is not the case and  $\int_{-\infty}^{+\infty} |\psi|^2 dx = \text{constant}$  then

$$\langle x \rangle = \frac{\int_{-\infty}^{+\infty} x |\psi|^2 dx}{\int_{-\infty}^{+\infty} |\psi|^2 dx}$$

Analogy: Consider identical particles distributed along the x-axis. There are  $N_1$  particles at  $x_1$ ,  $N_2$  particles at  $x_2$  ... etc

The average position is

$$\langle x \rangle = \frac{N_1 x_1 + N_2 x_2 + \dots}{N_1 + N_2 + \dots} = \frac{\sum N_i x_i}{\sum N_i}$$

→ In QM one replaces  $N_i$  by  $|\psi_i|^2$  where  $\psi_i$  is the wavefunction at  $x_i$ , & replace the sum by integration.

\*Momentum: With time the value  $\langle x \rangle$  evolves, due to time evolution of  $\psi$

$$\frac{d}{dt} \langle x \rangle = \frac{d}{dt} \int_{-\infty}^{\infty} x |\psi|^2 dx = \int x \frac{\partial}{\partial t} |\psi|^2 dx$$