



ENGINEERING PHYSICS

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ENGINEERING PHYSICS

Unit II : Quantum Mechanics of simple systems



Class # 22

- Hydrogen atom – a three dimensional analysis
- Wave equations in cartesian and spherical polar co-ordinates
- Method of solving a 3D wave equation
- Eigen functions and Energy eigen values
- Spectra of the Hydrogen atom

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Unit II : Quantum Mechanics of simple systems



➤ *Suggested Reading*

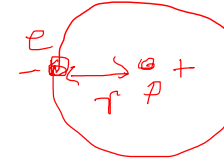
1. *Concepts of Modern Physics, Arthur Beiser, Chapter 6*
2. *Learning Material prepared by the Department of Physics*

➤ *Reference Videos*

1. *Video lectures : MIT 8.04 Quantum Physics I*
2. *Engineering Physics Class #19*

The Hydrogen atom problem

The Hydrogen atom is the simplest stable structure with a proton as the nucleus and a single electron bound to it



The Schrodinger's wave equation in x, y, z

$$\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \Psi(x, y, z) + (E - V) \Psi(x, y, z) = 0$$

The atom is spherically symmetric the solution of the SWE can be attempted using spherical polar co-ordinates.

The transition from the cartesian coordinate system to the spherical coordinate system -

$$x = r \sin \theta \cos \varphi ,$$

$$y = r \sin \theta \sin \varphi \text{ and}$$

$$z = r \cos \theta$$

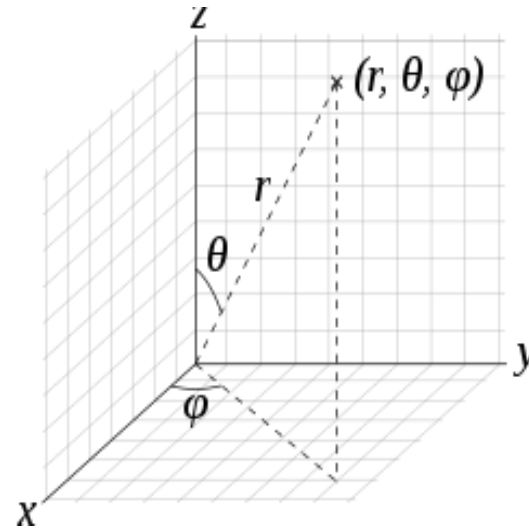
where

$$r = \sqrt{x^2 + y^2 + z^2} \text{ - the radius vector}$$

$$\theta = \tan^{-1} \left(\frac{\sqrt{x^2 + y^2}}{z} \right) \text{ the polar angle varies from } 0 \text{ to } 2\pi$$

and

$$\varphi = \tan^{-1} \left(\frac{y}{x} \right) \text{ - the azimuthal angle varies from } 0 \text{ to } 2\pi$$



Wave equation in spherical polar co-ordinates

The Schrodinger's wave equation in r, θ, φ

$$\frac{\hbar^2}{2\mu r^2 \sin \theta} \left[\sin \theta \frac{\partial}{\partial r} \left(r^2 \frac{\partial \Psi}{\partial r} \right) + \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Psi}{\partial \theta} \right) + \frac{1}{\sin \theta} \frac{\partial^2 \Psi}{\partial \varphi^2} \right] + (E - V(r)) \Psi(r, \theta, \varphi) = 0$$

where $\Psi(r, \theta, \varphi)$ is the wave function in spherical polar co-ordinate system

The wave function can be resolved into three independent components in the three independent variables r, θ and φ

$$\Psi(r, \theta, \varphi) = R(r) \cdot \Theta(\theta) \cdot \Phi(\varphi)$$

The SWE can be resolved into three independent wave equations in r, θ and φ

The Azimuthal and Angular wave equations in φ and θ

$$\frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial \varphi^2} = -m_l^2 \quad \text{with the solution}$$

$$\frac{\partial^2 \bar{\Phi}}{\partial \varphi^2} + m_l^2 \bar{\Phi} = 0$$

$\Phi(\varphi) = Ae^{im_l\varphi}$ where $m_l = 0, \pm 1, \pm 2, \dots$ is the magnetic quantum number

Substituting for the expression $\frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial \varphi^2} = -m_l^2$ we can separate the expressions in θ as

$$\frac{m_l^2}{\sin^2 \theta} - \frac{1}{\theta \sin \theta} \left[\frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta(\theta)}{\partial \theta} \right) \right] = l(l+1)$$

where l is an arbitrary constant which is an integer $\geq m_l$.

This puts a restriction on $m_l = 0, \pm 1, \pm 2, \dots, \pm l$

The radial wave equation

$l = 0, 1, 2, 3 \dots n - 1$ is the angular momentum quantum number

the quantized angular momentum of the orbital electron are

$$L = \sqrt{l(l+1)} \cdot \hbar$$

The radial part of the wave equation

$$\frac{1}{R} \left[\frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + \right] + \frac{2\mu r^2}{\hbar^2} [E - V(r)] = l(l+1)$$

The potential energy $V(r) = \frac{e^2}{4\pi\epsilon_0 r}$

the energy of the system is dependent only on the solution of the radial equation

The radial component of the wave function is

$$R_{nl}(r) = \frac{1}{r} \rho^{l+1} e^{-\rho} v(\rho)$$

The variable $\rho = \frac{r}{an}$ where n is an integer $n = 1, 2, 3..$ and

$$a \equiv \frac{4\pi\epsilon_0\hbar^2}{\mu e^2} = 0.529 \times 10^{-10} m \text{ is the Bohr radius}$$

$$v(\rho) = \sum_{j=0}^{j_{max}} c_j \rho^j \text{ is a polynomial of degree } j_{max} = n - l - 1$$

The coefficients of the polynomial terms are given by the recursion formula

$$\rho_0 = 2n$$

$$c_{j+1} = \left\{ \frac{2(j+l+1) - \rho_0}{(j+1)(j+2l+2)} \right\} c_j$$

The normalized radial wave function

$$R_{nl}(r) = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-l-1)!}{2n[(n+1)!]^3}} e^{-r/na} \left(\frac{2r}{na}\right)^l$$

where n is the principal quantum number $n = 1, 2, 3 \dots$

The first three state radial wave functions can be obtained with

$$n = 1 \text{ and } l = 0 \quad R_{10}(r) = 2a^{-3/2} e^{-r/a}$$

$$n = 2 \text{ and } l = 0 \quad R_{20}(r) = \frac{1}{\sqrt{2}} a^{-3/2} \left(1 - \frac{1}{2} \frac{r}{a}\right) e^{-r/2a}$$

$$n = 2 \text{ and } l = 1 \quad R_{21}(r) = \frac{1}{\sqrt{24}} a^{-3/2} \left(\frac{r}{a}\right) e^{-r/2a}$$

$$E_n \propto \frac{1}{n^2}$$

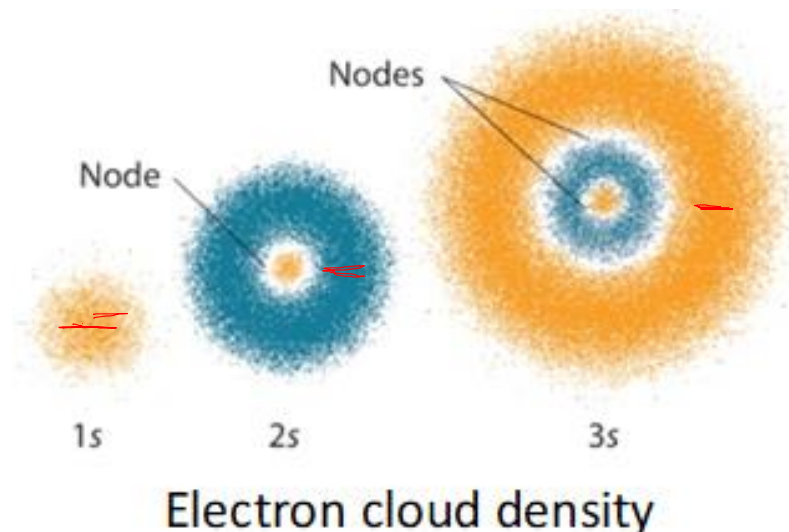
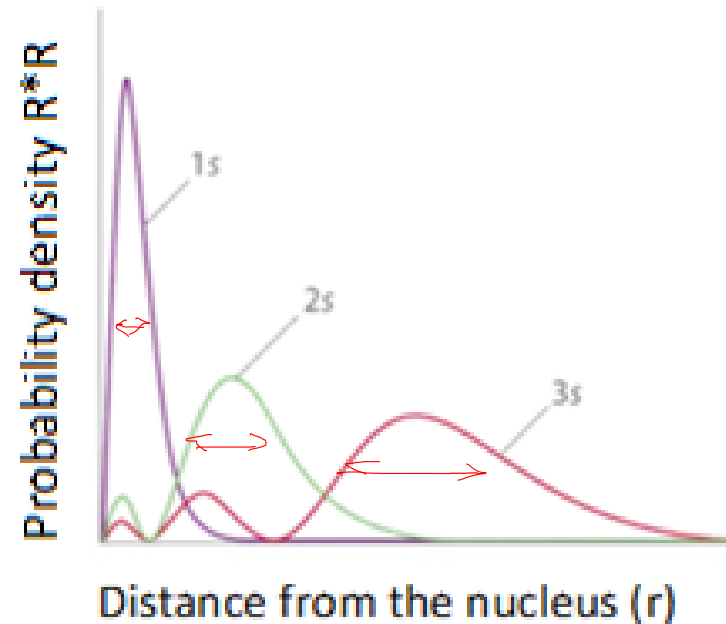
$$R^* R$$

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Probability density as a function of distance

The probability density plot as a function of distance r gives the most probable position of the electron

The electron cloud representation shows the probability of locating the electron in the three states 1s, 2s and 3s.



The energy of the electron in the different states can be written as

$$E_n = -\frac{\hbar^2 k^2}{2m} = -\frac{\mu e^4}{8\pi^2 \epsilon_0^2 \hbar^2 \rho_0^2} = -\frac{\mu e^4}{8\pi^2 \epsilon_0^2 \hbar^2 \cdot 4n^2}$$
$$E_n = -\left[\frac{\mu}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right] \frac{1}{n^2} = -\left[\frac{\mu}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right] \frac{1}{n^2}$$

where $n = 1, 2, 3$

The energy is written as negative to indicate that the system is in a bound state.

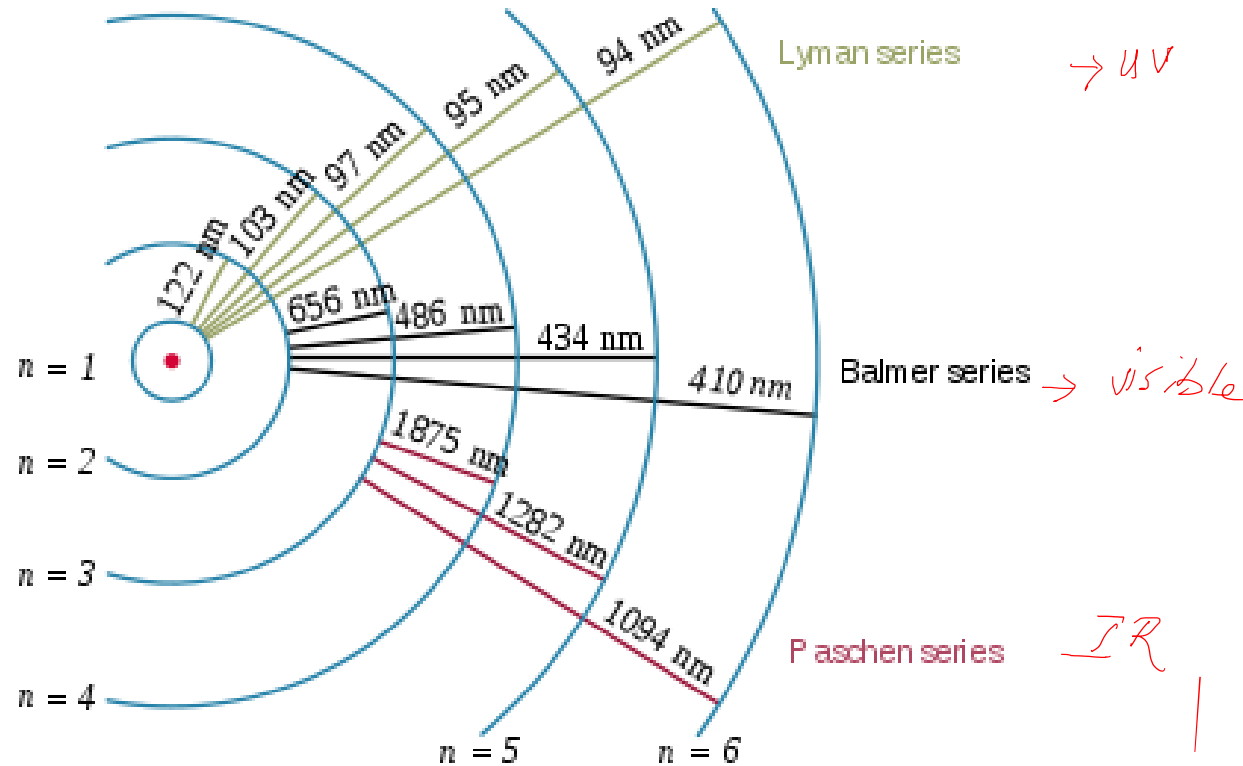
The ground state energy of the system can be evaluated as

$$E_1 = -\left[\frac{\mu}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right] = -13.6 \text{ eV} \quad E_2 = \frac{E_1}{4}$$

The energy difference between two states can be evaluated as

$$\begin{aligned}\Delta E &= E_{n2} - E_{n1} \\ &= - \left[\left\{ \frac{\mu}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_o} \right)^2 \right\} \frac{1}{n_1^2} - \left\{ \frac{\mu}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_o} \right)^2 \right\} \frac{1}{n_2^2} \right] \\ &= - \left\{ \frac{\mu}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_o} \right)^2 \right\} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]\end{aligned}$$

The energy of transition ΔE between different states gives us the absorption or emission spectra of the atom.



The predicted values of the wavelengths of the spectral lines of the Hydrogen atom $\left(\Delta E = \frac{hc}{\lambda}\right)$ agree with the observed wavelengths in the emission spectra of the Hydrogen atom.

The same analysis can be used to study hydrogen like atoms with a single electron in the outer most orbital such as Deuterium, doubly ionized Lithium, etc.

The effective mass μ can be estimated and gives reasonably correct values of the energy of the states and hence their spectral characteristics.

The concepts true of the concept of Hydrogen atom

1. The potential energy of seen by the electron is inversely proportional to the square of the distance
2. The Schrodinger's wave equation cannot be solved in the cartesian co-ordinate system
3. The wave equation in the azimuthal angle gives the angular momentum of the electron
4. The total quantum number of the electron $n = 1, 2, 3, \dots$
5. The electron can be excited to an energy state $> 13.6 \text{ eV}$
6. Excited electrons falling back to the state with $n=2$ gives out photons in the visible region.



THANK YOU

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