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ENGINEERING PHYSICS

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Class # 36

- Hydrogen atom – a 3D quantum system
- It is simply an electron electrostatically coupled to a proton
- As for other quantum systems we need to get the energy of this system.
- The first step is we need to solve the Schrodinger's equation as it is an eigen value equation
- We need to write the Schrodinger's equation in 3D

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

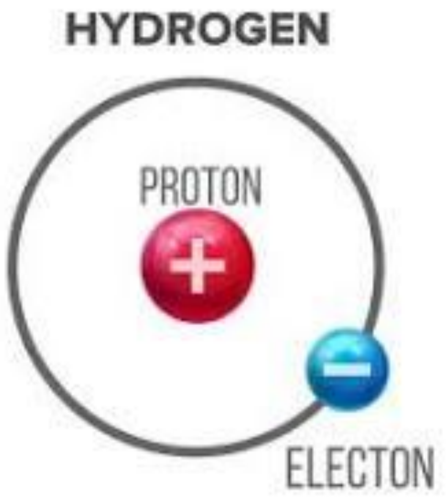
The Schrodinger's wave equation in x, y, z

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

What is expression for V?

$$V=-\frac{e^2}{4\pi\epsilon_0 r}$$

Where r is the electron-proton separation



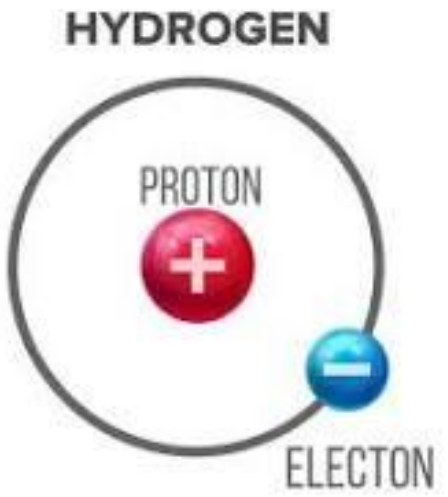
The Hydrogen atom problem

As the Schrodinger's equation is a partial differential equation we need to solve it by separation of variables. Thus we may think of expressing the wave function in terms of functions of x,y and z as follows

$$\psi(x,y,z) = X(x)Y(y)Z(z)$$

Things are fine until we come to the potential energy term $V = -\frac{e^2}{4\pi\epsilon_0 r} = -\frac{e^2}{4\pi\epsilon_0\sqrt{x^2+y^2+z^2}}$. *If we want to use separation of variables then we must separate the potential energy function as a sum of three functions each dependent on one variable, i.e.* $V(x,y,z) = V_1(x) + V_2(y) + V_3(z)$

We realize this is not possible. How then do we solve the Schrodinger's equation?

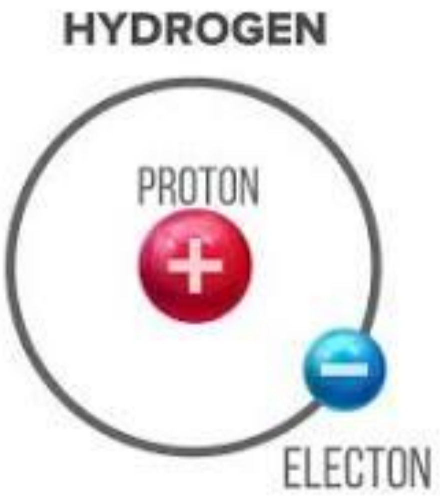


The Hydrogen atom problem

If we look at the expression for potential energy

$V = -\frac{e^2}{4\pi\epsilon_0 r}$ *we see that the potential energy only depends on the separation between the proton and electron and the value of the potential energy remains the same no matter how the separation "r" is oriented. The tip of "r" can move on a spherical surface and still V will be same. We call this spherically symmetric*

Then it boils down to view H-atom as a spherical system and we need to describe the position of the electron in such a system.



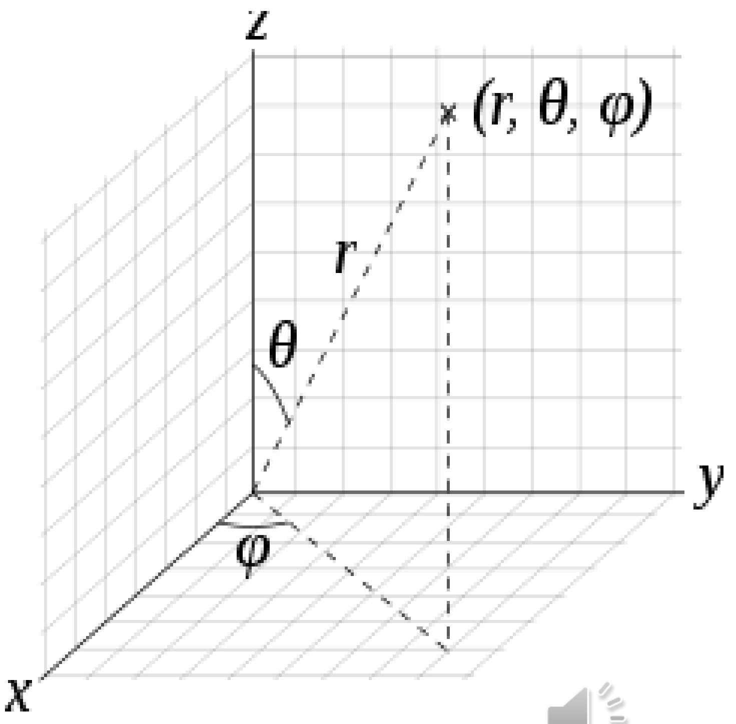
Spherical co-ordinate system

Just as for a cartesian system we need three coordinates to locate an electron(we assume that the proton is at the origin)

The three are

- *The distance of electron from proton – r*
- *The orientation r with respect to z-axis – ϑ (polar angle)*
- *The orientation of the plane containing r and z-axis with respect to x-axis – φ (azimuthal angle)*

The position of the electron is thus given by (r,ϑ,φ) see diagram. We call this system spherical polar system



Spherical co-ordinate system

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

$$x = r\sin\theta\cos\varphi\,,\;\; y = r\sin\theta\sin\varphi \;\text{ and }\; z = r\cos\theta$$

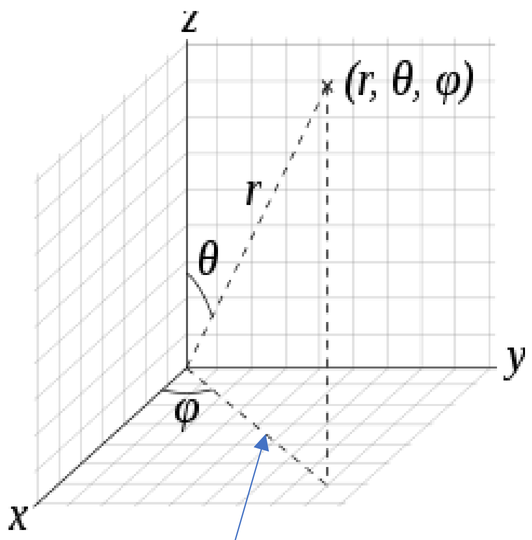
where

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

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

and

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



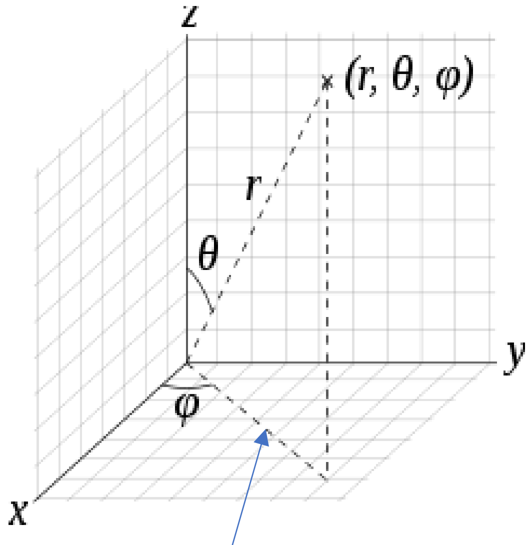
r sin (θ)

Concept of reduced mass

Before we write the Schrodinger's equation in the spherical polar system there is one more issue to consider.
For a moment let us revisit the Schrodinger's equation in cartesian system

$$\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\Psi(x,y,z)+\left(E+\frac{e^2}{4\pi\varepsilon_0\sqrt{x^2+y^2+z^2}}\right)\Psi(x,y,z)=0$$

Here ψ actually describes the combined electron-proton system and hence is a function of 6 coordinates – 3 for electron and 3 for proton. The Schrodinger's equation has to represent this and which is complicated.



r sin (θ)

Concept of reduced mass

A simple way out of this is to consider the proton, located at the origin to be infinitely heavy, the price we pay is to consider the reduced mass of the electron denoted by μ.

The expression for the reduced mass is $\mu = \frac{Mm}{M+m}$, *where M is the mass of the proton and m the mass of the electron*

The expression can be rewritten as $\mu = \frac{m}{1+\frac{m}{M}}$. *Suppose the proton has an infinite mass then we see that* $\mu = m$.

Schrodinger's equation using reduced mass

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The Schrodinger's equation, written in terms of reduced mass is now

$$\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\Psi(x,y,z)$$

$$+\left(E+\frac{e^2}{4\pi\varepsilon_0\sqrt{x^2+y^2+z^2}}\right)\Psi(x,y,z)=0$$

Now $\Psi(x,y,z)$ describes only the electron

We now proceed to write the Schrodinger's equation in spherical polar coordinates and see for ourselves what is the advantage.

Wave equation in spherical polar co-ordinates

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

$$\frac{1}{r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial r}\right)+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Psi}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2\Psi}{\partial\varphi^2}\right]$$

$$+\frac{2\mu}{\hbar^2}\left(E+\frac{e^2}{4\pi\varepsilon_0 r}\right)\Psi(r,\theta,\varphi)=0$$

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

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

Now we see the advantage – the potential energy term has only one variable 'r' and hence can be taken together with the other r dependent terms

Solutions to SWE

Using separation of variables, the Schrodinger's wave equation is written as

$$\frac{1}{r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial R\Theta\Phi}{\partial r}\right)+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial R\Theta\Phi}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 R\Theta\Phi}{\partial\varphi^2}\right]$$

$$+\frac{2\mu}{\hbar^2}\left(E+\frac{e^2}{4\pi\varepsilon_0 r}\right)R\Theta\Phi = 0$$ *which when simplified is*

$$\frac{1}{r^2}\left[\Theta\Phi\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{R\Phi}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\frac{R\Theta}{\sin^2\theta}\frac{d^2\Phi}{d\varphi^2}\right]$$

$$+\frac{2\mu}{\hbar^2}\left(E+\frac{e^2}{4\pi\varepsilon_0 r}\right)R\Theta\Phi = 0$$

which then becomes $\frac{1}{r^2}\Theta\Phi\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{R\Phi}{r^2\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\frac{R\Theta}{r^2\sin^2\theta}\frac{d^2\Phi}{d\varphi^2}$

$$+\frac{2\mu}{\hbar^2}\left(E+\frac{e^2}{4\pi\varepsilon_0 r}\right)R\Theta\Phi = 0.$$

Solution to Schrodinger's equation

Dividing by $R\Theta\Phi$ we get

$$\frac{1}{Rr^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{1}{\Theta r^2\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\frac{1}{\Phi r^2\sin^2\theta}\frac{d^2\Phi}{d\varphi^2}$$

$$+\frac{2\mu}{\hbar^2}\left(E+\frac{e^2}{4\pi\varepsilon_0 r}\right)=0$$

Multiplying throughout by $r^2\sin^2\theta$ we get

$$\frac{sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\frac{1}{\Phi}\frac{d^2\Phi}{d\varphi^2}$$

$$+\frac{2\mu r^2 sin^2\theta}{\hbar^2}\left(E+\frac{e^2}{4\pi\varepsilon_0 r}\right)=0$$

Solution to Schrodinger's equation

$$\frac{sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\frac{1}{\Phi}\frac{d^2\Phi}{d\varphi^2}$$

$$+\frac{2\mu r^2 sin^2\theta}{\hbar^2}\left(E+\frac{e^2}{4\pi\varepsilon_0 r}\right)=0$$

Moving the φ dependent term to the other side of the equation

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\varphi^2}=-\left[\frac{sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\frac{2\mu r^2 sin^2\theta}{\hbar^2}\left(E+\frac{e^2}{4\pi\varepsilon_0 r}\right)\right]$$

The LHS is a function of ϕ whereas the RHS is a function of r and θ. Hence both must be equal to some constant which is taken as $-m_l^2$

Solving for LHS: $\frac{1}{\Phi}\frac{d^2\Phi}{d\varphi^2}=-m_l^2$, with the solution $\Phi(\varphi)=Ae^{im_l\varphi}$

where $m_l=0,\pm1,\pm2,\ldots$ .is the magnetic quantum number

Solution to Schrodinger's equation

The RHS is now $\frac{sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\frac{2\mu r^2 sin^2\theta}{\hbar^2}\left(E+\frac{e^2}{4\pi\varepsilon_0 r}\right)= m_l^2$

We can separate the r dependent terms and θ dependent terms to get

$$\frac{sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2\mu r^2}{\hbar^2}\left(E+\frac{e^2}{4\pi\varepsilon_0 r}\right)=\frac{m_l^2}{sin^2\theta}-\frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)$$

Each side is now equal to another constant written as l(l+1)

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

$$\frac{sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2\mu r^2}{\hbar^2}\left(E+\frac{e^2}{4\pi\varepsilon_0 r}\right)=l(l+1)$$

Solution to Schrodinger's equation

The solutions to the θ dependent equation is

$\Theta_{lm_l} = sin^{m_l}(\theta)\, F_{lm_l}(cos\theta)$ where F is a polynomial

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

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

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

Normalised radial wave functions

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 $n = 1, 2, 3 \ldots$

The first three state radial wave functions can be obtained with

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

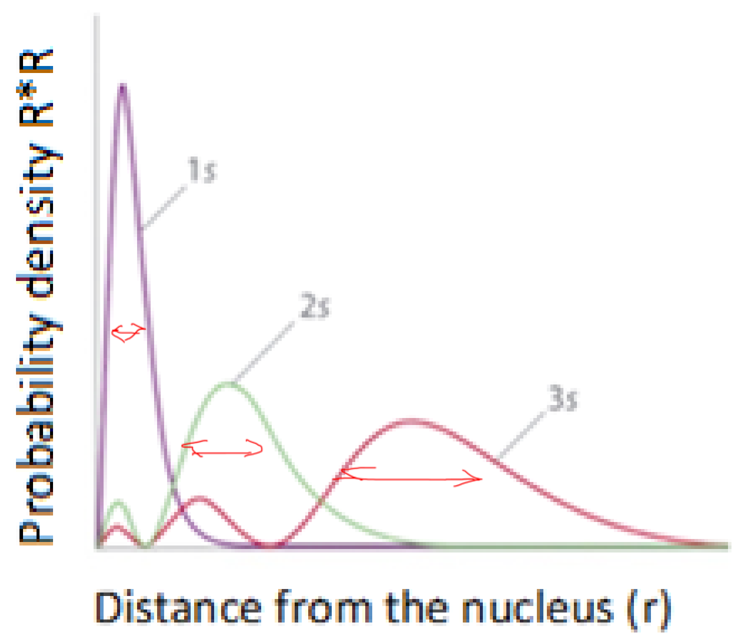
$n = 2 \; and \; l = 0 \qquad R_{20}(r) = \frac{1}{\sqrt{2}} a^{-3/2} \left(1 - \frac{1}{2}\frac{r}{a}\right) e^{-r/2a}$

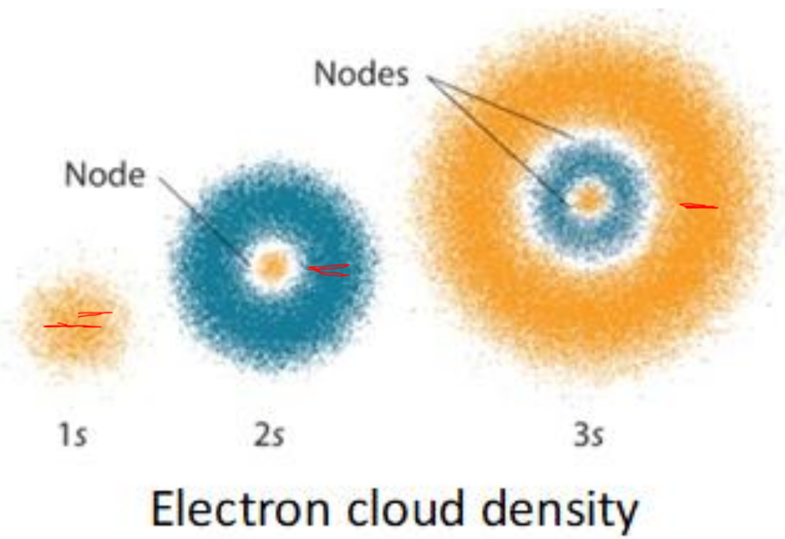
$n = 2 \; and \; l = 1 \qquad R_{21}(r) = \frac{1}{\sqrt{24}} a^{-3/2} \left(\frac{r}{a}\right) e^{-r/2a}$

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.





Eigen energy values

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

$$E_n = -\frac{\hbar^2 k^2}{2m} = -\frac{\mu e^4}{8\pi^2 \varepsilon_o^2 \hbar^2 \rho_o^2} = -\frac{\mu e^4}{8\pi^2 \varepsilon_o^2 \hbar^2 . 4n^2}$$

$$E_n = -\left[\frac{\mu}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_o}\right)^2\right]\frac{1}{n^2} = -\left[\frac{\mu}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_o}\right)^2\right]\frac{1}{n^2}$$

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

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

The energy difference between two states can be evaluated as

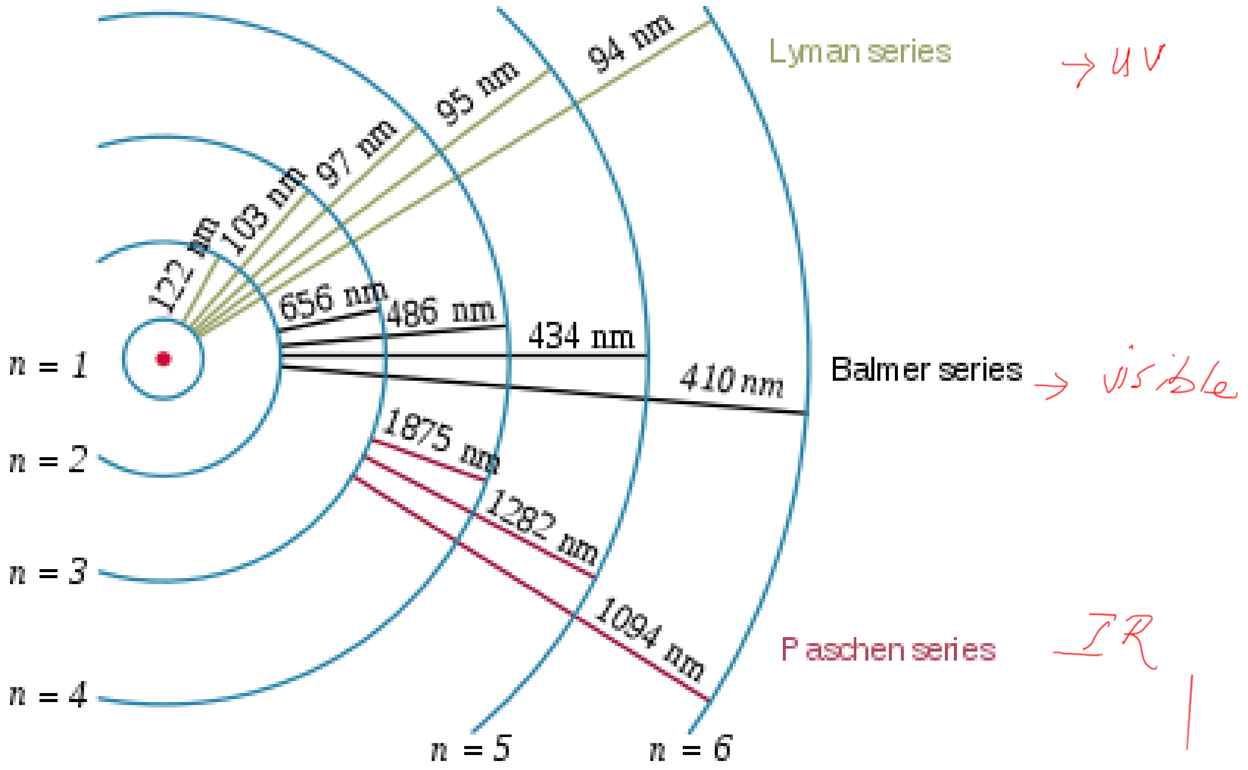
$$\Delta E = E_{n2} - E_{n1}$$

$$= -\left[\left\{\frac{\mu}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_o}\right)^2\right\}\frac{1}{n_1^2} - \left\{\frac{\mu}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_o}\right)^2\right\}\frac{1}{n_2^2}\right]$$

$$= -\left\{\frac{\mu}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_o}\right)^2\right\}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

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

Hydrogen atom spectra



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.

Hydrogenic atoms

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.

THANK YOU

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