

CH107: Week 2 & 3

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1 Hydrogen Atom

Schrodinger Equation for Hydrogen atom will be of the form

$$\left[-\frac{\hbar^2}{2m_N} \nabla_N^2 - \frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{QZe^2}{r_{eN}} \right] \Psi_{Total} = E_{Total} \cdot \Psi_{Total} \quad (1)$$

We can convert this equation into frame of reference of Centre of mass. Eqn(1) converts to. Note that the potential energy term remains unchanged in the conversion :

$$\left[-\frac{\hbar^2}{2M} \nabla_N^2 - \frac{\hbar^2}{2\mu} \nabla_e^2 - \frac{QZe^2}{r} \right] \Psi_{Total} = E_{Total} \cdot \Psi_{Total} \quad (2)$$

Where $M = m_e + m_N$ and $\mu = \frac{m_e m_N}{m_e + m_N}$

Here the equation can be divided into two parts: Nucleic hamiltonian and electronic hamiltonian:

$$\hat{H} = \hat{H}_N + \hat{H}_e, \quad \Psi_{Total} = \chi_N \cdot \psi_e, \quad E_{Total} = E_N + E_e$$

$$\hat{H}_N \cdot \chi_N = \left(-\frac{\hbar^2}{2M} \nabla_N^2 \right) \chi_N = E_N \chi_N \quad (3)$$

$$\hat{H}_e \cdot \psi_e = \left(-\frac{\hbar^2}{2\mu} \nabla_e^2 - \frac{QZe^2}{r} \right) \psi_e = E_N \chi_N \quad (4)$$

The nuclear part behaves just like a free particle which we have discussed earlier. Under this condition it is not possible to separate this equation into three different variables so we define a new co-ordinate system.

2 Spherical Coordinate System

Here we replace x,y,z by r, θ, ϕ . $\mathbf{z} = r \cos \theta, \mathbf{x} = r \sin \theta \cos \phi, \mathbf{y} = r \sin \theta \sin \phi$ where $r \in (0, \infty), \theta \in [0, \pi], \phi \in (0, 2\pi]$. $d\mathbf{r} = d\mathbf{x} \cdot d\mathbf{y} \cdot d\mathbf{z} = r^2 \cdot d\mathbf{r} \cdot \sin \theta \cdot d\theta \cdot d\phi$ On solving we find that schrodinger's equation for electronic part in spherical polar coordinates is, substituting these values in eqn(4) we get:

$$\frac{\hbar^2}{2\mu} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi_e}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi_e}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi_e}{\partial \phi^2} \right] - \frac{QZe^2}{r} \psi_e = E_e \cdot \psi_e \quad (5)$$

Now we can perform separation of variables by substituting ψ_e as $R \cdot \Theta \cdot \Phi$ and rearranging a few terms we can get 3 equations:

$$\frac{1}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + \frac{2\mu r QZe^2}{\hbar^2} + \frac{2\mu r^2}{\hbar^2} E_e = \beta \quad (6)$$

$$\frac{1}{\Theta \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta}{\partial \theta} \right) + \beta \sin^2 \theta = m^2 \quad (7)$$

$$\frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial \phi^2} = -m^2 \quad (8)$$

Here β and m are constant values which would be subject to constraints because of the boundary conditions. eqn(6) is the radial part of the function and eqn(7) and (8) represent the angular part of the wave function.

3 Quantum Numbers

Solution to ϕ part

We can guess the solution to be $\Phi(\phi) = Ae^{\pm im\phi}$ but since the wave function has to be continuous and ϕ varies from 0 to 2π , $\Phi(\phi + 2\pi) = \Phi(\phi)$ which restricts $m \in \mathbb{Z}$. We can also relate the **angular momentum along z direction** with \mathbf{m} using the momentum operator and simplifying which gives

$$\hat{L}_Z \Phi = \frac{\hbar}{i} \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \Phi = \frac{\hbar}{i} \frac{\partial \Phi}{\partial \phi} = \frac{\hbar}{i} im \Phi = m \hbar \Phi \quad (9)$$

This leads to space quantization.

The Θ part:

We can solve the θ equation using complex mathematical techniques. The solution involves the use of Associated Legendre Polynomials $P_l^m(\cos\theta)$. From the boundary conditions, a new quantum number is introduced: **l : Azimuthal Quantum Number** and $l \in \mathbb{W}$. Also $\beta = l(l+1)$. Further the expression also involves the term $\frac{(l-m)!}{(l+m)!}$ which further restricts the value of $|m| \leq l$.

The angular($\Theta \cdot \Phi$) part of the solution $Y_l^m(\theta, \phi) = \Theta \cdot \Phi$ are called the **Spherical harmonics**.

Also it can be shown that the **total angular momentum** operator \hat{L}^2 is related to the angular part of the wave function such that:

$$\hat{L}^2 Y(\theta, \phi) = \hbar^2 l(l+1) Y(\theta, \phi) \quad (10)$$

The R part: The solution to the R part introduces a new quantum number $n \in \mathbb{N}$ and restricts the value of $l < n$. The value ' n ' is known as **Principal Quantum Number**

The **Energy** obtained from full quantum mechanical treatment is similar to the energy obtained from Bohr's model.

We finally have the **four quantum number**: **n**: Specifies Energy of electron, **l**: Specifies magnitude of total angular momentum, **m**: Specifies the orientation of electron's orbital momentum and **s**: Specifies the orientation of the electron's spin angular momentum.

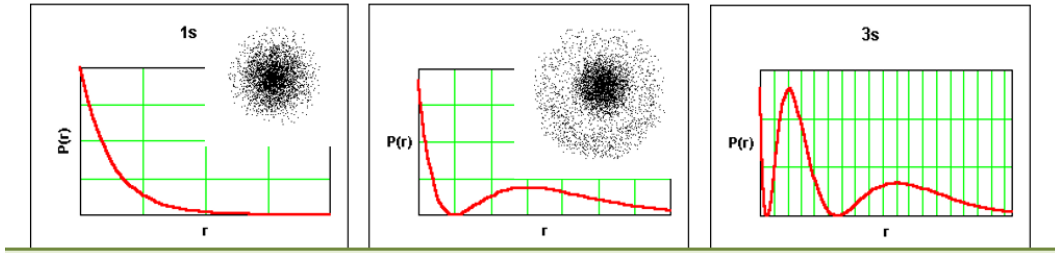
4 Hydrogen Wave Function

3 quantum numbers are required to describe the 3D system of orbital completely. Also unlike PIB, the 3 quantum numbers are inter-related.

We then studied the various Spherical harmonics for various orbitals for $n = 1, 2, \dots, l = 0, 1, 2, 3$ and $m = 0, \pm 1, \pm 2$. We also studied various radial functions for the same orbitals. According to the radial function the number of **radial nodes** turned out to be $n - l - 1$. The complete wavefunction is $\psi_{n,l,m}(r, \theta, \phi) = R_{n,l}(r) \cdot Y_l^m(\theta, \phi)$. For example:

$$\psi_{2,1,+1} = \frac{1}{8\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left(\frac{r}{a_0}\right)^{3/2} e^{-\frac{r}{2a_0}} \sin\theta e^{i\phi} \quad (11)$$

Orbitals: Orbitals is defined as an 1-electron wavefunction. We then studied in detail the Radial Wavefunction of s-orbitals for hydrogen atoms for $n = 1, 2, \dots$. These graphs are exponential in nature. These are graphs of $R^2(r) - r$.



But these graphs do not represent the probability of finding electrons at the given positions. Instead it represents the **probability density** of the electron at that distance.

Probability: Volume element in spherical coord: In order to find the probability of finding electron at required position we need to multiply probability density function by the volume element dV . The volume element is a spherical shell of thickness dr at distance r from the nucleus and it is equal to $4\pi r^2 dr$. We finally plotted the radial **probability distribution functions** ($4\pi r^2 R^2(r)$) of $l = 0$ (s orbital) as follows.

