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Quantum Mechanics & Applications
Chapter - 4
Quantum Theory of Hydrogen Like Atoms

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Quantum Theory of Hydrogen-like Atoms

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Syllabus: Time independent Schrodinger equation in spherical polar coordinates; separation of variables for second order partial differential equation; angular momentum operator & quantum numbers; Radial wavefunction from Frobenius method; shapes of the probability densities for ground and first excited states; Orbital angular momentum quantum numbers 1 and m; s, p, d,...shells.

Q 1. Write down the time independent schrodinger equation in spherical polar co-ordinates.

Ans. In the three dimensions, the time-independent schrodinger equation takes the form

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

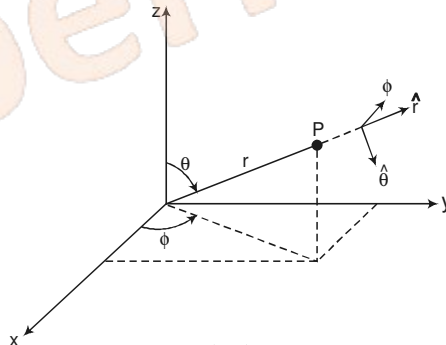
If the potential of the physical to be examined is spherically symmetric, then the schrodinger equation in spherical polar coordinates can be used to advantage. For a three - dimensional problem, the laplacian in spherical polar coordinates is used to express the schrodinger equation in the condensed form

$$\frac{-\hbar^2}{2m} \nabla^2 \Psi + U(r, \theta, \phi) \psi(r, \theta, \phi) = E \Psi(r, \theta, \phi)$$

Expanded, it takes the form

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

This is the form best suited for the study of the zhydrogen atom.



Q 2. Solve the Schrodinger equation for Hydrogen like atom.

The solution of the Schrodinger equation for the hydrogen atom is a formidable mathematical problem, but is of such fundamental importance that it will be treated in outline here. The solution is managed by separating the variables so that the wave functions is represented by the product:

$$\Psi(r, \theta, \phi) = R(r) P(\theta) F(\phi)$$

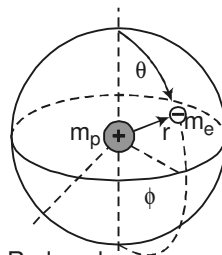
\swarrow \swarrow \downarrow
 n ℓ m_ℓ
 principal orbital magnetic
 quantum quantum quantum
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The separation leads to three equations for the three spatial variables, and their solutions give rise to three quantum numbers associated with the hydrogen energy levels.

Hydrogen Schrodinger Equation

The electron in the hydrogen atom sees a spherically symmetric potential, so it is logical to use spherical polar coordinates to develop the schrodinger equation. The potential energy is simply that a point charge.

$$U(r) = \frac{-e^2}{4\pi\epsilon_0 r}$$



Reduced mass

$$\mu = \frac{m_e m_p}{m_e + m_p}$$

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The expanded form of the schrodinger equation is shown below. Solving it involves separating the variables onto the form

$$\Psi(r, \theta, \phi) = R(r)P(\theta)F(\phi)$$

The starting point is the form of the schrodinger equation.

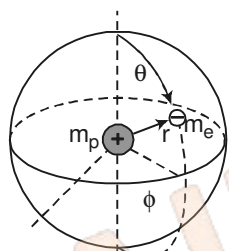
$$\frac{-\hbar^2}{2\mu} \frac{1}{\sin\theta} \left[\sin\theta \frac{\partial}{\partial r} \left(r^2 \frac{\partial \Psi}{\partial r} \right) + \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial \Psi}{\partial \theta} \right) + \frac{1}{\sin\theta} \frac{\partial^2 \Psi}{\partial \phi^2}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

$$+U(r)\Psi(r, \theta, \phi) = E\Psi(r, \theta, \phi)$$

Quantum Numbers From Hydrogen Equations

The hydrogen atom solution requires finding solutions to the separated equations which obey the constraints on the wavefunction. The solution to the radial equation can exist only when a constant which arises in the solution is restricted to integer values. This gives the principal quantum number:

$$P(r) \quad \left\{ \begin{array}{l} \text{Solution exists} \\ \text{if and only if....} \end{array} \right. \rightarrow n = 1, 2, 3, \dots$$



Reduced mass

$$\mu = \frac{m_e m_p}{m_e + m_p}$$

Similarly, a constant arises in the colatitude equation which gives the orbital quantum number:

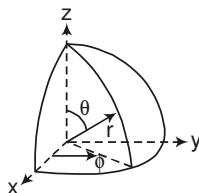
$$P(\theta) \quad \left\{ \begin{array}{l} \text{Solution exists} \\ \text{if and only if....} \end{array} \right. \rightarrow l = 0, 1, 2, 3, \dots, n - 1$$

Finally, constraints on the azimuthal equation give what is called the magnetic quantum number:

$$F(\phi) \quad \left\{ \begin{array}{l} \text{Solution exists} \\ \text{if and only if....} \end{array} \right. \rightarrow m_l = -l, -l + 1, \dots, +l$$

Quantum Numbers, Hydrogen Atom

In the solution to the Schrodinger for the hydrogen atom, three quantum numbers arise from the space geometry of the solution and a fourth arises from electron spin. No two electrons can have an identical set of quantum numbers according to the Pauli exclusion principle, so the quantum numbers set building up of the periodic table of the elements.



The three spherical coordinates are associated with the three spatial quantum numbers.

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$R(r)$ Principal quantum number $n = 1, 2, 3, \dots$

$P(\theta)$ Orbital quantum number $l = 0, 1, 2, \dots, n - 1$

$F(\phi)$ Magnetic quantum number

$m_l = -l, -l + 1, \dots, 0, \dots, l - 1, l$ or $2l + 1$ values



Spin quantum number $m_s = +\frac{1}{2}, -\frac{1}{2}$

Separating the Hydrogen Equation

One of the approaches to solving a partial differential equation is to separate it into individual equations for each variable involved. The hydrogen schrodinger equation is separable, and collecting all the radius-dependent terms and setting them equal to a constant gives the radial equation:

$$\frac{1}{R} \frac{d}{dr} \left[r^2 \frac{dR}{dr} \right] + \frac{2\mu}{\hbar^2} (Er^2 + ke^2 r) = l(l+1)$$

Then the angular parts of the equation can be separated into a colatitude equation:

$$\frac{\sin \theta}{p} \frac{d}{d\theta} \left[\sin \theta \frac{dp}{d\theta} \right] + C_r \sin^2 \theta = -C_\phi$$

and an azimuthal equation.

$$\frac{1}{F} \frac{d^2 F}{d\phi^2} = C_\phi$$

Its detailed step wise solution is in solved paper 2017.

Q 3. Explain Orbital angular momentum quantum numbers- l and m of s, p, d, f shells?

Ans.

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Upon separation of the schrodinger equation for the hydrogen atom, the colatitude equation is:

$$\frac{\sin \theta}{p} \frac{d}{d\theta} \left[\sin \theta \frac{dp}{d\theta} \right] + C_r \sin^2 \theta = -C_\phi$$

The solution of the azimuthal equation provides the constraint

$$C_\phi = -m_\ell^2 \quad \text{Support by Donating}$$

A detailed solution involves conversion of the above equation to a form in which the variable is $\cos \theta$. It can be solved by a series expansion (polynomial) method in which the conditions for a solution force the remaining constant to be of the form

$$C_r = \ell(\ell+1)$$

producing the orbital quantum number. The solutions to the colatitude equation are in a form called associated Legendre functions, and when

properly normalized form part of the hydrogen wavefunctions. Form constraints on the hydrogen wavefunction in the colatitude equation arises a constant of the form

$$\ell(\ell+1) \text{ where } \ell = -0, 1, 2, 3, \dots, n-1$$

where n is the principal quantum number. This defines the orbital quantum number, which determines the magnitude of the orbital angular momentum in the relationship

$$L^2 = \ell(\ell+1)\hbar^2$$

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This relationship between the magnitude of the angular momentum and the quantum number is commonly visualized in terms of a vector model. The orbital quantum number determines the bounded on the magnetic quantum number. The orbital quantum number is used as a part of the designation of atomic electron state in the spectroscopic notation.

$\ell = 0$	<i>For example, if $n = 2, \ell = 1$</i>
$\ell = 1$	<i>the state is designated $2p$</i>
$\ell = 2$	
$\ell = 3$	

The orbital quantum number plays a role in the Seaman interaction since the orbital motion contributes a magnetic moment, and is important as an indicator of sub shell difference in electron energies.

Spectroscopic Notation

Before the nature of atomic electron states was clarified by the application of quantum mechanics, spectroscopists saw evidence of distinctive series in the spectra of atoms and assigned letters to the characteristic spectra. In terms of the quantum number designations of electron states, the notation is as follows:

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	$n = 1$	$n = 2$	$n = 3$	$n = 4$
<i>s -- sharp</i> $\ell = 0$	1s	2s	3s	4s
<i>p -- principal</i> $\ell = 1$		2p	3p	4p
<i>d -- diffuse</i> $\ell = 2$			3d	4d
<i>f -- fundamental</i> $\ell = 3$				4f
<i>g</i>		$\ell = 4$	<i>beyond this point, the notation</i>	
<i>h</i>		$\ell = 5$	<i>just follows the alphabet</i>	

