

Module – 2 "Atomic physics and atomic structure"

Lecture 7 Quantum Mechanical treatment of One-electron atoms

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Objectives

In this lecture, we will apply the Schrodinger Equation to the simple system “Hydrogen” and compare the outcome of the Quantum Theory with the experimental results obtained from different experiments.

We will also get to know about the “wavefunction” and its use in developing the concept of the structure of atoms.

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Why hydrogen?

⇒ One electron atom and the simplest bound system in nature

⇒ Referring to the adjacent figure -1, the proton (+ve Charge) is at the center and the electron (-ve charge) is moving around the center.

⇒ The attractive force between them is Coloumbic in nature and the potential is

$$V = V(x, y, z) = \frac{-Ze^2}{4\pi\epsilon_0\sqrt{x^2 + y^2 + z^2}}$$

....**Equation -1**

Where Z is the charge of the nucleus,

$Z = 1$ for hydrogen.

⇒ Since it is a two body problem, we convert it to one body problem by introducing reduced mass

$$\mu = \frac{mM}{m + M}$$

Where m and M are the masses of the electron and proton, respectively.

⇒ So, the total energy of the system = kinetic energy + potential energy

$$\frac{1}{2\mu}(p_x^2 + p_y^2 + p_z^2) + V(x, y, z) = E \quad \text{..... Equation -2}$$

Here, p_x , p_y , and p_z are the linear momenta and E is the total energy.

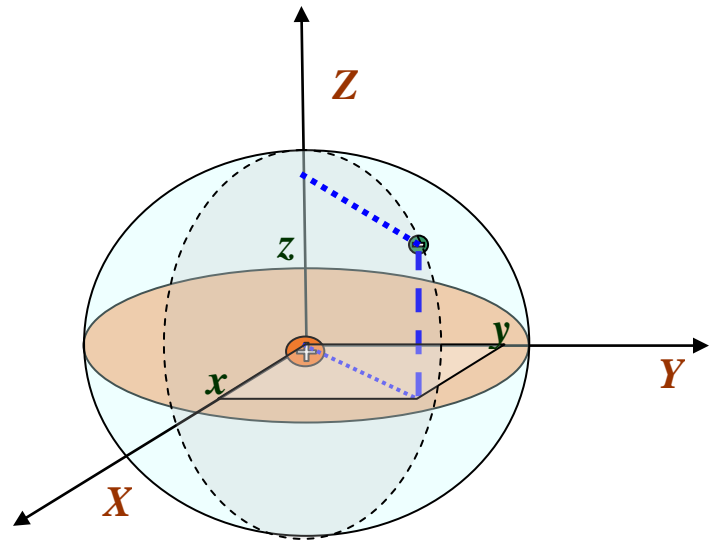


Figure - 1

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⇒ For the quantum mechanical treatment, we will convert the classical dynamical quantities (p_x , p_y , and p_z) to its corresponding quantum mechanical operators

$$p_x \rightarrow -i\hbar \frac{\partial}{\partial x}, p_y \rightarrow -i\hbar \frac{\partial}{\partial y}, p_z \rightarrow -i\hbar \frac{\partial}{\partial z}$$

$$E \rightarrow i\hbar \frac{\partial}{\partial t}$$

⇒ Substituting in Equation – 2, we get

$$-\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V(x, y, z) = i\hbar \frac{\partial}{\partial t} \dots\dots\dots \text{Equation -3}$$

⇒ Here, we introduce the WAVEFUNCTION to represent the electron.

$$\Psi = \Psi(x, y, z, t) \dots\dots\dots \text{Equation -4}$$

The wavefunction contains the information about the position and the time evolution of the electronic motion. We will understand more about this later.

So operating equation -2, on the wavefunction, $\Psi = \Psi(x, y, z, t)$,

$$\begin{aligned} & -\frac{\hbar^2}{2\mu} \left(\frac{\partial^2 \Psi(x, y, z, t)}{\partial x^2} + \frac{\partial^2 \Psi(x, y, z, t)}{\partial y^2} + \frac{\partial^2 \Psi(x, y, z, t)}{\partial z^2} \right) + V(x, y, z) \Psi(x, y, z, t) = i\hbar \frac{\partial \Psi(x, y, z, t)}{\partial t} \\ \Rightarrow & -\frac{\hbar^2}{2\mu} \nabla^2 \Psi + V\Psi = i\hbar \frac{\partial \Psi}{\partial t} \\ & \dots\dots\dots \text{Equation -5} \end{aligned}$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad \text{is the Laplacian operator.}$$

This Equation -5 is known as Time dependent Schrodinger Equation.

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Since the potential $V(x, y, z)$ does not depend on time t , and we are interested to evaluate the energy of the stationary (time independent) states, we can take this wavefunction as the explicit dependence of time such as

$$\Psi(x, y, z, t) = \psi(x, y, z) e^{-iEt/\hbar}$$

Substituting this to Equation -5, we get

$$-\frac{\hbar^2}{2\mu} \nabla^2 \psi(x, y, z) + V\psi(x, y, z) = E\psi(x, y, z) \dots \dots \dots \text{Equation -6}$$

This is the Time Independent Schrodinger Equation.

Now we have to evaluate the stationary state energies (E) of the electron in this system by solving this equation to explain the observed spectra of hydrogen.

Since the potential is spherically symmetric

$$V(x, y, z) = \frac{Ze^2}{4\pi\epsilon_0 \sqrt{x^2 + y^2 + z^2}} = \frac{Ze^2}{4\pi\epsilon_0 r} = V(r)$$

We can convert Equation -6 to its spherical polar coordinate (Figure -2) form,

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

..... Equation -7

Radial distance $\Rightarrow r$, Polar angle $\Rightarrow \theta$ and

Azimuthal angle $\Rightarrow \phi$

The form of the Laplacian operator in Spherical polar coordinates is

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}$$

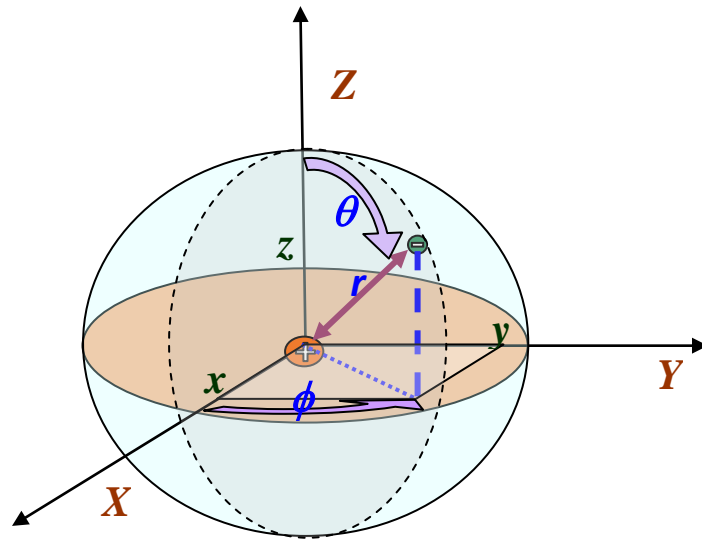


Figure - 2

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Using the separation of the variables, we can write the wavefunction as the product form of the independent variables $R(r), \Theta(\theta), \Phi(\phi)$

$$\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$$

Substituting in equation – 7,

$$-\frac{\hbar^2}{2\mu} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R\Theta\Phi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial R\Theta\Phi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 R\Theta\Phi}{\partial \phi^2} \right] + V(r) R\Theta\Phi = ER\Theta\Phi$$

Carrying out the partial differentiation,

$$-\frac{\hbar^2}{2\mu} \left[\frac{\Theta\Phi}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + \frac{R\Phi}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta}{\partial \theta} \right) + \frac{R\Theta}{r^2 \sin^2 \theta} \frac{\partial^2 \Phi}{\partial \phi^2} \right] + V(r) R\Theta\Phi = ER\Theta\Phi$$

Multiplying the this equation by $\frac{-2\mu r^2}{R\Theta\Phi \hbar^2}$ and rearranging we get,

$$\left[\frac{1}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + \frac{1}{\Theta \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta}{\partial \theta} \right) + \frac{1}{\Phi \sin^2 \theta} \frac{\partial^2 \Phi}{\partial \phi^2} \right] + \frac{2\mu r^2}{\hbar^2} [E - V(r)] = 0$$

Separating the radial ($R(r)$) and angular ($\Theta(\theta), \Phi(\phi)$) part

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

Note here that the partial derivative forms are converted to total derivative form. Now each equation should be equal to a constant, let's take as λ .

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So, the radial part is

$$\frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2\mu r^2}{\hbar^2} [E - V(r)] = \lambda$$
$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \left[\frac{2\mu}{\hbar^2} (E - V(r)) - \frac{\lambda}{r^2} \right] R = 0 \quad \dots\dots\dots \text{Equation -8}$$

And the angular part is

$$\frac{1}{\Theta \sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \frac{1}{\Phi \sin^2 \theta} \frac{d^2 \Phi}{d\phi^2} = -\lambda$$
$$\Rightarrow \frac{\sin \theta}{\Theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = -\lambda \sin^2 \theta \quad \dots\dots\dots \text{Equation -9}$$

Now, separating the polar and the azimuthal part

$$\frac{\sin \theta}{\Theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \lambda \sin^2 \theta = -\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = m_l^2 \quad \dots\dots\dots \text{Equation -10}$$

Here, we have taken that both sides should be equal to a constant m^2 . Note that we have three independent equations from equation 9 and 10.

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Now let us first consider the azimuthal part (**Equation -10**)

$$-\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = m_l^2$$

$$\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} + m_l^2 \Phi = 0$$

The general solution of this equation may be written in the form

$$\Phi_{m_l}(\phi) = \frac{1}{\sqrt{2\pi}} e^{im_l \phi} \dots\dots\dots \text{Equation -11}$$

Which satisfies the orthonormality condition $\int_0^{2\pi} \Phi_{m_l}^*(\phi) \Phi_{m_l'}(\phi) d\phi = \delta_{m_l m_l'}$

As the eigen functions must be single valued, i.e., $\Phi(0) = \Phi(2\pi)$ which means

$$e^{im_l 0} = e^{im_l 2\pi}$$

And using Euler's formula $1 = \cos(m_l 2\pi) + i \sin(m_l 2\pi)$

This is satisfied only if $m_l = 0, \pm 1, \pm 2, \dots$

Therefore, acceptable solutions only exist when m_l can only have certain integer values, i.e. it is a quantum number. Thus, m_l is called the magnetic quantum number in spectroscopy because it plays role when atom interacts with magnetic fields.

Now we will discuss the polar part in **Equation 10**

$$\frac{\sin \theta}{\Theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \lambda \sin^2 \theta = m_l^2$$

Rearranging, we get

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta(\theta)}{d\theta} \right) + \left(\lambda - \frac{m_l^2}{\sin^2 \theta} \right) \Theta(\theta) = 0 \quad \text{..... Equation -}$$

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Let us introduce new variable $\omega = \cos \theta$, the **Equation-12** becomes,

$$\frac{d}{d\omega} \left((1 - \omega^2) \frac{d\Theta(\omega)}{d\omega} \right) + \left(\lambda - \frac{m_l^2}{1 - \omega^2} \right) \Theta(\omega) = 0 \quad \text{..... Equation -13}$$

The **Equation-13** has singularities at $\omega = \pm 1$, which may be eliminated by having a solution Θ in the form of

$$\Theta = (1 - \omega^2)^{s/2} u$$

Then **Equation-13** becomes

$$(1 - \omega^2) \frac{d^2 u}{d\omega^2} - 2\omega(s+1) \frac{du}{d\omega} + \left[\lambda + \frac{s^2 \omega^2 - m_l^2}{1 - \omega^2} \right] u = 0$$

Which can be written as

$$(1 - \omega^2) \frac{d^2 u}{d\omega^2} - 2\omega(s+1) \frac{du}{d\omega} + \left[\lambda - s^2 - s + \frac{s^2 - m_l^2}{1 - \omega^2} \right] u = 0 \quad \text{..... Equation -14}$$

The last singular term in Equation-14 can be removed by taking $s = \pm m_l \geq 0$, and then we have

$$(1 - \omega^2) \frac{d^2 u}{d\omega^2} - 2\omega(m_l + 1) \frac{du}{d\omega} + [\lambda - m_l(m_l + 1)]u = 0 \dots\dots\dots \text{Equation -15}$$

Which is a regular equation and hence its series solution may be written as

$$u = \sum_{r=0} a_r \omega^r \dots\dots\dots \text{Equation -16}$$

Substituting in Equation-15, yields the recursion relation

$$a_{r+2} = \frac{(r + m_l)(r + m_l + 1) - \lambda}{(r + 1)(r + 2)} a_r$$

Requiring that the series be (Equation-16) be limited by a certain power $r = q$, i.e. requiring that it be a polynomial of order q , we have to introduce the condition

$$a_{r+2} = 0, a_r \neq 0 \text{ which requires } \lambda = (q + m_l)(q + m_l + 1)$$

Where $q = 0, 1, 2, 3, \dots$

Now we introduce $l = q + m_l = 0, 1, 2, 3, \dots$ (orbital quantum number) such that

$$l \geq m_l$$

$$\lambda = l(l + 1)$$

Then Equation-12 becomes

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta(\theta)}{d\theta} \right) + \left(l(l+1) - \frac{m_l^2}{\sin^2 \theta} \right) \Theta(\theta) = 0 \dots\dots\dots \text{Equation - 17}$$

This is well known associated Legendre differential equation with its solution as associated Legendre polynomials

$$\Theta_{l,m_l} = C_l^{m_l} P_l^{m_l}(\omega) \dots\dots\dots \text{Equation -18}$$

Where $C_l^{m_l}$ is the normalization factor and $P_l^{m_l}(\omega)$ is the associated Legendre polynomial defined by

$$\begin{aligned} P_l^{m_l} &= (1-\omega^2)^{m_l/2} \frac{d^{l+m_l}}{d\omega^{l+m_l}} \left[\frac{(\omega^2-1)^l}{2^l l!} \right] \\ &= (1-\omega^2)^{m_l/2} \frac{d^{m_l}}{d\omega^{m_l}} P_l(\omega) \end{aligned}$$

Where $P_l(\omega)$ is the ordinary Legendre Polynomial. This expression holds for negative values of m_l also

$$P_l^{m_l}(\omega) = (-1)^{m_l} \frac{(l+m_l)!}{(l-m_l)!} P_l^{-m_l}(\omega)$$

From this we can establish the range of variation of the azimuthal (magnetic) quantum number $m_l = 0, \pm 1, \pm 2, \pm 3, \dots, \pm l$

The associated Legendre Polynomials satisfy the orthonormalization property

$$\int_{-1}^1 P_l^{m_l}(\omega) P_l^{m_l}(\omega) d\omega = \frac{2}{2l+1} \frac{(l+m_l)!}{(l-m_l)!} \delta_{l,l'}$$

So,

$$C_l^{m_l} = \sqrt{\frac{2l+1}{2} \frac{(l-m_l)!}{(l+m_l)!}}$$

Then Equation-18 becomes

$$\Theta_{l,m_l} = \sqrt{\frac{2l+1}{2} \frac{(l-m_l)!}{(l+m_l)!}} P_l^{m_l}(\omega) \dots\dots\dots \text{Equation -19}$$

So, we have now two quantum numbers, namely, Orbital (l) and magnetic (m_l)

$$l = 0, 1, 2, 3, \dots$$

$$m_l = -l, -l+1, \dots, 0, \dots, l-1, l$$

Depending of the value of l and m_l , some of the Associated Legendre polynomials are

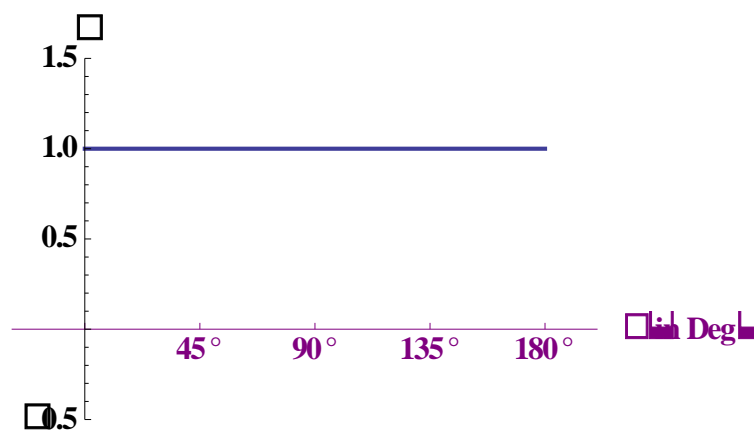
$$P_0^0 = 1$$

$$P_1^0 = \cos \theta \quad P_1^{\pm 1} = (1 - \cos^2 \theta)^{1/2}$$

$$P_2^0 = 1 - 3 \cos^2 \theta \quad P_2^{\pm 1} = (1 - \cos^2 \theta)^{1/2} \cos \theta$$

$$P_2^{\pm 2} = 1 - \cos^2 \theta$$

These functions are



Now, we can have the total angular part, from **Equation-11 and -19**

$$\begin{aligned}
 Y_l^{m_l}(\theta, \phi) &= \Theta_{l, m_l}(\theta) \Phi_{m_l}(\phi) \\
 &= \sqrt{\frac{2l+1}{4\pi} \frac{(l-m_l)!}{(l+m_l)!}} P_l^{m_l}(\cos \theta) e^{im_l \phi} \\
 &\dots\dots\dots \textbf{Equation -20}
 \end{aligned}$$

Recap

In this lecture, we have learnt the quantum mechanical treatment of hydrogen atom problem.

To do this, we have used the separation of variables method and in this method we have written the total wavefunction as a product function of the radial part and the angular part.

Since the coulomb interaction between the nucleus and the electron is radially symmetric, we have solved the angular part separately.

While solving the angular part of the wavefunction, we have introduced two quantum numbers namely, azimuthal or orbital quantum number l and magnetic quantum number m_l .

(****Check the symbol in the lecture*****)

In the next lecture we will solve the radial part of the wavefunction and will construct the total wavefunction of the hydrogen atom. We will also calculate the energy levels of the hydrogen atom and will compare it with the observed spectrum.