

## Module 1 : Atomic Structure

### Lecture 4 : The Schrodinger Equation

#### Objectives

In this lecture you will learn the following

- Write the Schrodinger equation for hydrogen atom
- Separate the  $\nabla^2$  (Laplacian) operator in polar coordinates  $r$ ,  $\theta$  and  $\phi$  and write the separate equations in the variables  $r$ ,  $\theta$  and  $\phi$ .
- Relate the quantization of  $n$ ,  $l$  and  $m_l$  to the boundary conditions.
- Rationalize the relations between  $n$ ,  $l$  and  $m_l$ .

#### 4.1 Introduction

In the lecture 2, we have seen that the quantum mechanical description of a particle moving in one, two and three dimensions brings out the essential aspects of operators, wave functions and boundary conditions. The hydrogen atom represents the simplest atomic system in which an electron moves in three-dimensions under the influence of the nuclear charge of  $+e = 4.8 \times 10^{-10}$  e.s.u. We shall examine the quantum mechanical structure of the hydrogen atom in considerable detail as it provides important insights regarding the structure of multi-electron atoms, molecules and solids.

The Schrodinger equation for hydrogen atom can be written as,

$$\left( \frac{-h^2}{8\pi^2 m} \right) \left\{ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right\} \Psi - \left( \frac{e^2}{4\pi \epsilon_0 r} \right) \Psi = E\Psi \quad (4.1a)$$

or

$$-\left( \frac{h^2}{8\pi^2 m} \right) \nabla^2 \Psi - \left( \frac{e^2}{4\pi \epsilon_0 r} \right) \Psi = E\Psi \quad (4.1b)$$

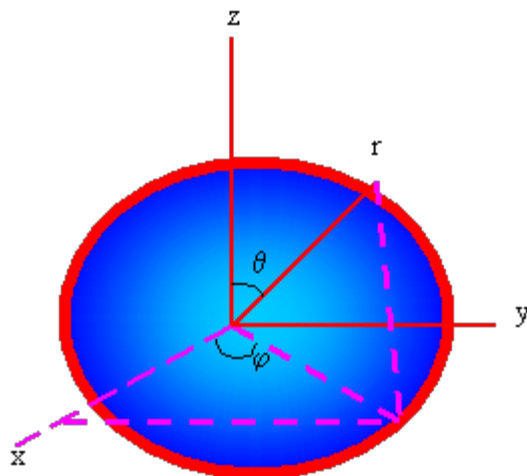
$$\nabla^2 = \left\{ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right\} \text{ (Cartesian coordinates)}$$

$$\nabla^2 = (1/r) \left( \partial^2 / \partial r^2 \right) r + (1/r^2) (1/\sin^2 \theta) \left( \partial^2 / \partial \phi^2 \right) + (1/\sin \theta) \left( \partial / \partial \theta \right) \sin \theta \left( \partial / \partial \theta \right) \quad (4.1c)$$

$\theta$ ) (Spherical polar coordinates)

The potential energy term arises from the Coulombic interaction between the electron (charge of  $-e$ ) and the proton (charge of  $+e$ ) and separated by a distance ' $r$ '. ( $\epsilon_0$  is the permittivity of vacuum. We have written the coulombic interaction in MKS units here, so that you will be familiar with both the MKS and the CGS units used later.) The Schrodinger equation for the hydrogen atom has been solved exactly i.e; the solutions can be expressed in terms of standard mathematical / analytical functions. The energies predicted by the equation match with the experimentally observed energy levels.

In view of the spherical symmetry of the atom, it is more convenient to use spherical coordinates ( $r, \theta$  and  $\phi$ ) rather than Cartesian coordinates ( $x, y, z$ ) in the description of the system. The relation between the spherical and Cartesian coordinates is illustrated in Figure 4.1



**Figure 4.1 Cartesian and spherical polar coordinate systems**

The solution to (4.1) can be written as the product of a radial part  $R$  and an angular part  $Y(\theta, \phi)$ . The angular part can further be written as a product of two functions, one, of the polar angle and the other of the azimuthal angle.

$$\Psi(r, \theta, \phi) = R(r) Y(\theta, \phi) = R(r) \Theta(\theta) \Phi(\phi) \quad (4.2)$$

Equation 4.1 cannot be separated into three equations in which each equation depends on  $x$  or  $y$  or  $z$ . Such a separation was possible for a particle in a box wherein the potential  $V$  was zero. In the hydrogen atom, the potential depends only on  $r$ . Therefore, the Schrodinger Equation 4.1 takes the following form in terms of the variables  $r, \theta$  and  $\phi$ .

$$\frac{\partial^2 \Phi}{\partial \phi^2} + m_l^2 \Phi = 0 \quad (4.3)$$

$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Theta}{\partial \theta} \right) - \frac{m^2}{\sin^2 \theta} \Theta + l(l+1) \Theta = 0 \quad (4.4)$$

$$\frac{1}{r} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R}{\partial r} \right) - \frac{l(l+1)}{r^2} R + \frac{8\pi^2 m}{h^2} \left( E + \frac{Ze^2}{4\pi\epsilon_0 r} \right) = 0 \quad (4.5)$$

The first equation, Eq. (4.3) corresponds to an ordinary second order differential equation similar to Eq. (2.1). Equations 4.4 and 4.5 are a little harder to solve and you will learn how to solve them in your mathematics courses.

The solutions to these are listed in Table (4.1) and you may like to verify that the radial part ( $R = R_{nl}(r)$  where subscripts indicate quantum numbers) satisfies Eq. 4.5 while the angular part  $Y(\theta, \phi) = \Theta(\theta) \cdot \Phi(\phi)$  jointly satisfies Eqns (4.3) and (4.4), i.e, the functions depending on  $\theta$  (e.g.  $\cos^2 \theta$  or  $\cos \theta$  or  $\cos \theta \sin \theta$ ) of Table 4.1 satisfy equation Eq. (4.4) while the functions of  $\phi$  (e.g.  $e^{im\phi}$  or  $e^{-im\phi}$ ) satisfy Eq.(4.3).

$$\phi(i.e. \cos m\phi \text{ or } \sin m\phi) \quad \pm m\phi$$

The formula for energy E of Eq. (4.5) is:  $-[Z^2 e^4 m_e / 8 \epsilon_0^2 h^2] (1/n^2)$  which is the same as Bhor's result. For the hydrogen atom, E depends only on the principal quantum number n.

For the present, we shall first list the solutions (see Table 4.1) and study their implications in detail. Although the graphs of these functions are given later, try to plot them yourself so that you are quite at ease with their usage.

Table 4.1: Angular and radial parts of hydrogen-atom (and hydrogen - like atom) wave-functions

Angular part $Y(\theta, \phi) = \Theta(\theta) \Phi(\phi)$	Radial part $R_{nl}(r)$
$Y(s) = \left(\frac{1}{4\pi}\right)^{1/2}$	$R(1s) = 2\left(\frac{Z}{a_0}\right)^{3/2} e^{-\sigma/2}$
$Y(p_x) = \left(\frac{3}{4\pi}\right)^{1/2} \sin\theta \cos\phi$	$R(2s) = \frac{1}{2\sqrt{2}} \left(\frac{Z}{a_0}\right)^{3/2} (2 - \sigma) e^{-\sigma/2}$
$Y(p_y) = \left(\frac{3}{4\pi}\right)^{1/2} \sin\theta \sin\phi$	$R(2p) = \frac{1}{2\sqrt{6}} \left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2}$
$Y(p_z) = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$	
$Y(d_{z^2}) = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$	
$Y(d_{zx}) = \left(\frac{15}{4\pi}\right)^{1/2} \sin\theta \cos\theta \sin\phi$	$R(3s) = \frac{1}{9\sqrt{3}} \left(\frac{Z}{a_0}\right)^{3/2} (6 - 6\sigma + \sigma^2) e^{-\sigma/2}$
$Y(d_{yz}) = \left(\frac{15}{4\pi}\right)^{1/2} \sin\theta \cos\theta \sin\phi$	$R(3p) = \frac{1}{9\sqrt{6}} \left(\frac{Z}{a_0}\right)^{3/2} (4 - \rho) \rho e^{-\rho/2}$
$Y(d_{xy}) = \left(\frac{15}{4\pi}\right)^{1/2} \sin^2\theta \sin 2\phi$	$R(3d) = \frac{1}{9\sqrt{30}} \left(\frac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/2}$
$Z = \text{atomic number,}$ $\sigma = \frac{2Zr}{na_0}; a_0 = \frac{1}{4\pi^2} \frac{h^2}{m_e e^2}$	

As may be expected from the earlier discussion of a particle in a three-dimensional box, three quantum numbers emerge from the application of the boundary conditions, namely that  $\Psi$  is single valued, continuous and finite. The energy  $E$  of Eq 4.5 depends explicitly on  $n$  and the quantum numbers  $m_l$  and  $l$  explicitly appear only in Eqs. 4.3 and 4.4.

The quantum numbers are

$n$ , where  $n = 1, 2, 3, \dots$

$l$ , where  $l = 0, 1, 2, \dots, n-1$

$m_l$ , where  $m_l = l, l-1, l-2, \dots, 0, \dots, -1, -2, \dots, -l$

The energy of the electron in a multielectron atom is expected to depend on the combination of all three quantum numbers, but in view of the fact that the hydrogen atom has only one electron, the energy depends only on the quantum number ' $n$ ' which is therefore called principal quantum number. The quantum number ' $l$ ' is called the angular momentum quantum number and determines the angular momentum and hence the rotational kinetic energy of the electron. Since the angular kinetic energy cannot exceed the total energy of the electron, the values which ' $l$ ' can take, are restricted from above by the values of ' $n$ '. The third quantum number,  $m_l$  is called the magnetic quantum number. For  $l > 0$ , the angular momentum can project with different components in a given direction.

The number of projections is given by  $2l + 1$ . The range of values which  $m_l$  can take is governed by the value of ' $l$ '. The electron also has a spin and therefore should be considered as a tiny magnet. In presence of an external magnetic field, the spin can interact by aligning (lowering of energy) with the magnetic field if the spin is in one direction. The opposite alignment results in an increase in the energy. Thus, a fourth quantum number must be introduced to define the spin of the electron. Since there can be only two directions of spin, 'clockwise' and 'anti-clockwise', the spin quantum number  $m_s$  can take values  $+\frac{1}{2}$  or  $-\frac{1}{2}$ . The electron is a quantum mechanical object and not a sphere. There is no classical analogue of a spinning electron and the words spin, clockwise and anticlockwise should not be taken literally. No one has actually "seen" a spinning electron!

## 4.2 Problems

4.1) What are the formulae for the normalized radial parts of 1s and 2s orbitals of  $\text{He}^+$ ,  $\text{Na}^{10+}$  and  $\text{U}^{91+}$  ions? Which one of them decays fastest with increasing  $r$ ?

4.2) From the five solutions for the H - atom for  $n=3$ ,  $l=2$  and  $m_l = -2, -1, 0, 1$  and  $2$  (ie, the 5 d orbitals), construct functions which are real by suitable combinations of the complex components consisting of the  $e^{\pm im_l \phi}$  terms

4.3) Verify that the functions  $\cos^2 \theta$  and  $(3\cos^2 \theta - 1)$  satisfy the angular part of the Schrodinger equation for the H- atom.

4.4) Verify that  $e^{-\rho/2}$  and  $\rho e^{-\rho/2}$  (where  $\rho = 2Zr/na_0$ ) satisfy the radial part of the schrodinger equation for the H-atom. Notice that we have used  $\rho$  instead of sigma ( $\sigma$ ) used in Table 4.1.

4.5) What is the asymptotic form of the radial part ( for each  $n$  ) of the schrodinger equation for large  $r$ ?

4.6) For  $\Psi = e^{-\rho/2}$ , what is the value of energy in the schrodinger equation for the H-atom? Substitute the value of all the constants and obtain the numerical value of this energy.

## Recap

In this lecture, you have learnt the following

## Summary

In the present lecture you have been introduced to the Schrodinger equation for a hydrogen atom. The potential energy between the nucleus and electron depends on the distance  $r$  between them. Since  $r =$

$(x^2 + y^2 + z^2)$  can not be separated in terms of  $x$ ,  $y$ , and  $z$ , the kinetic energy operator which includes  $\nabla^2$  is separated in spherical polar coordinates  $r$ ,  $\theta$  and  $\phi$  and in these coordinates the Schrodinger equation is separable. The three separate equations in the variables  $r$ ,  $\theta$  and  $\phi$  (Equations 4.3, 4.4 and 4.5) can be solved and the solutions  $\Psi(r, \theta, \phi) = R_{nl}(r) \Theta(\theta) \Phi(\phi)$  are listed in Table 4.1.

The detailed techniques for solving the  $r$  part and  $\theta$  part will be introduced in a later course in mathematics. For the present you may substitute the solutions into the equations and verify that you get the correct values of energy and quantum numbers.

The integer values and the relationships between  $n$ ,  $l$  and  $m_l$  (ie  $l < n$ ,  $|m_l| \leq l$ ) are a consequence of the boundary conditions and the uncertainty principle.