

## Chapter 5 Atomic Levels

### 5-1 Orbiting

In this chapter we shall study the atomic level by studying the levels of the simple hydrogen atom and the Hydrogen like atoms. Hydrogen atom picture is a proton fixed at the origin and an electron of reduced mass  $\mu$  interacting with the proton through a Coulomb potential

$$U(r) = -\frac{e^2}{4\pi\epsilon_0 r} \quad 1)$$

Here  $e$  is the charge of the electron and  $\epsilon_0$  is the permittivity of free space and  $r$  is the distance between the electron and the proton. The model suggests that we use a spherical coordinate system with the proton at the origin. The Schrödinger equation for a hydrogen atom is

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

Where

$$\frac{-\hbar^2}{2\mu} \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right)_{\theta, \phi} + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right)_{r, \phi} + \frac{1}{r^2 \sin^2 \theta} \left( \frac{\partial^2}{\partial \phi^2} \right)_{r, \theta} \right] + U(r)\psi(r, \theta, \phi) = E\psi(r, \theta, \phi) \quad 3)$$

At first sight, this partial differential equations looks exceedingly complicated. To bring Eq.3 into more manageable form, first multiply thought  $2\mu r^2$  to obtain

$$-\hbar^2 \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right)_{\theta, \phi} - \hbar^2 \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right)_{r, \phi} + \frac{1}{\sin^2 \theta} \left( \frac{\partial^2 \psi}{\partial \phi^2} \right)_{r, \theta} \right] + 2\mu r^2 [U(r) - E]\psi(r, \theta, \phi) = 0 \quad 4)$$

The second term here (the one containing only  $\theta$  and  $\phi$ ) is the square of the angular momentum defined before thus we can write the equation as

$$-\hbar^2 \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) - L^2 \psi + 2\mu r^2 [U(r) - E]\psi(r, \theta, \phi) = 0 \quad 5)$$

Only the second term here depends on  $\theta$  and  $\phi$ .

$$\hat{L}^2 Y_l^m(\theta, \phi) = \hbar^2 l(l+1) Y_l^m(\theta, \phi)$$

Consequently if we let

$$\psi(r, \theta, \phi) = R(r) Y_l^m(\theta, \phi) \quad (6)$$

And using square of the angular momentum Eq.5 can be written as

$$\frac{-\hbar^2}{2\mu r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \left[ \frac{\hbar^2 l(l+1)}{2\mu r^2} + U(r) - E \right] R(r) = 0 \quad (7)$$

This equation is known as the radial equation and the only new equation that we have to study in order to have a complete solution to the hydrogen atom. The solution to this equation depends on the two numbers  $n$  and  $l$  are given by

$$R_{nl}(r) = - \left[ \frac{(n-l-1)!}{2n[(n+l)!]^3} \right]^{1/2} \left( \frac{2}{na_0} \right)^{l+3/2} r^l e^{-r/na_0} L_{n+l}^{2l+1} \left( \frac{2r}{na_0} \right) \quad (8)$$

Where  $L_{n+l}^{2l+1} \left( \frac{2r}{na_0} \right)$  are called the associated Laguerre functions. The first few associated Laguerre functions are given in the table below

$n = 1; l = 0$	$L_1^1(x) = -1$	$x = \frac{2r}{a_0}$
$n = 2; l = 0$ ; $l = 1$	$L_2^1(x) = -2!(2-x)$ $L_3^3(x) = -3!$	$x = \frac{r}{a_0}$
$n = 3; l = 0$ ; $l = 1$ ; $l = 2$	$L_3^1(x) = -3! \left( 3 - 3x + \frac{1}{2}x^2 \right)$ $L_4^3(x) = -4!(4-x)$ $L_5^5(x) = -5!$	$x = \frac{2r}{3a_0}$
$n = 4; l = 0$ ; $l = 1$ ; $l = 2$ ; $l = 3$	$L_4^1(x) = -4! \left( 4 - 6x + 2x^2 - \frac{1}{6}x^3 \right)$ $L_5^3(x) = -5! \left( 10 - 5x + \frac{1}{2}x^2 \right)$ $L_6^5(x) = -6!(6-x)$ $L_7^7(x) = -7!$	$x = \frac{r}{2a_0}$

The complete hydrogen atomic wave function is

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)Y_l^m(\theta, \phi)$$

$$\psi_{nlm}(r, \theta, \phi) = \left( - \left[ \frac{(n-l-1)!}{2n[(n+l)!]^3} \right]^{1/2} \left( \frac{2}{na_0} \right)^{l+3/2} r^l e^{-r/na_0} L_{n+l}^{2l+1} \left( \frac{2r}{na_0} \right) \right) \left( \left[ \frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!} \right]^{1/2} P_l^{|m|}(\cos\theta) e^{im\phi} \right) \quad (9)$$

The normalization condition for the hydrogen atomic wave function is

$$\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \int_0^{\infty} dr r^2 \psi_{nlm}^*(r, \theta, \phi) \psi_{nlm}(r, \theta, \phi) = 1$$

Because H is Hermitian must be orthogonal and the orthogonality condition is given by

$$\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \int_0^{\infty} dr r^2 \psi_{nlm}^*(r, \theta, \phi) \psi_{n'l'm'}(r, \theta, \phi) = \delta_{nn'} \delta_{ll'} \delta_{mm'}$$

It is clear that the hydrogen atomic wave function depends on **three quantum numbers**,

n: is called the principal quantum numbers and have the values  $n=1,2,3,\dots$ . The energy depends only on it

$$E_n = -\frac{e^2}{8\pi\epsilon_0 a_0 n^2} \quad (10)$$

l: is called the angular momentum quantum number and has the values  $0,1,\dots,n-1$ . The angular momentum of the electron about the proton is determined completely by  $l$  through

$$|L| = \hbar\sqrt{l(l+1)} \quad (11)$$

It is customary to denote the value of  $l$  by a letter shown in the table

$l =$	0	1	2	3	Higher values
Corresponding letter	S Sharp	P Principal	d diffuse	F fundamental	Alphabetic sequence following f

$m$ : is called the magnetic quantum number and it takes on  $2l+1$  values, because the energy of the hydrogen atom in a magnetic field depends on  $m$  through

$$L_z = m\hbar$$

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$n = 1; l = 0, m = 0$	$\psi_{100} = \frac{1}{\sqrt{\pi}} \left( \frac{Z}{a_o} \right)^{\frac{3}{2}} e^{-\sigma}$
$n = 2; l = 0, m = 0$ $; l = 1, m = 0$ $; l = 1, m = \pm 1$	$\psi_{200} = \frac{1}{\sqrt{32\pi}} \left( \frac{Z}{a_o} \right)^{\frac{3}{2}} (2 - \sigma) e^{-\sigma/2}$ $\psi_{210} = \frac{1}{\sqrt{32\pi}} \left( \frac{Z}{a_o} \right)^{\frac{3}{2}} \sigma e^{-\sigma/2} \cos \theta$ $\psi_{21\pm 1} = \frac{1}{\sqrt{64\pi}} \left( \frac{Z}{a_o} \right)^{\frac{3}{2}} \sigma e^{-\sigma/2} \sin \theta e^{\pm i\phi}$
$n = 3; l = 0, m = 0$  $; l = 1, m = 0$  $; l = 1, m = \pm 1$  $; l = 2, m = 0$  $; l = 2, m = \pm 1$  $; l = 2, m = \pm 2$	$\psi_{300} = \frac{1}{81\sqrt{3\pi}} \left( \frac{Z}{a_o} \right)^{\frac{3}{2}} (27 - 18\sigma + 2\sigma^2) e^{-\sigma/3}$ $\psi_{310} = \frac{1}{81} \left( \frac{2}{\pi} \right)^{\frac{1}{2}} \left( \frac{Z}{a_o} \right)^{\frac{3}{2}} (6\sigma - \sigma^2) \sigma e^{-\sigma/3} \cos \theta$ $\psi_{31\pm 1} = \frac{1}{81\sqrt{\pi}} \left( \frac{Z}{a_o} \right)^{\frac{3}{2}} (6\sigma - \sigma^2) e^{-\sigma/3} \sin \theta e^{\pm i\phi}$ $\psi_{320} = \frac{1}{81\sqrt{6\pi}} \left( \frac{Z}{a_o} \right)^{\frac{3}{2}} (\sigma^2) e^{-\sigma/3} (3 \cos^2 \theta - 1)$ $\psi_{32\pm 1} = \frac{1}{81\sqrt{\pi}} \left( \frac{Z}{a_o} \right)^{\frac{3}{2}} \sigma^2 e^{-\sigma/3} \sin \theta \cos \theta e^{\pm i\phi}$ $\psi_{32\pm 2} = \frac{1}{162\sqrt{\pi}} \left( \frac{Z}{a_o} \right)^{\frac{3}{2}} \sigma^2 e^{-\sigma/3} \sin^2 \theta e^{\pm 2i\phi}$

**For the case  $l = 0$  (only s orbitals is available)**

Is the simplest case, and the radial function associated with the 1s state is (Note:  $Z=1$ )

**Example 1:**

Find the complete Hydrogen wave function of the first hydrogen atomic level 1s and find the probability that the electron lies on it?

**Solution:**

$$\psi_{1s}(r, \theta, \phi) = R_{10}(r)Y_0^0(\theta, \phi)$$

$$R_{1s}(r) = \frac{2}{a_0^{3/2}} e^{-r/a_0}$$

$$\text{And } Y_0^0(\theta, \phi) = \frac{1}{\sqrt{4\pi}}$$

And the complete 1s wave function is

$$\psi_{1s}(r, \theta, \phi) = R_{10}(r)Y_0^0(\theta, \phi) = (\pi a_0^3)^{-1/2} e^{-r/a_0}$$

The probability that the electron lies between  $r$  and  $r+dr$  is obtained by integrating

$$prob(1s) = \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \int_0^{\infty} dr r^2 \psi_{1s}^*(r, \theta, \phi) \psi_{1s}(r, \theta, \phi) = \frac{4}{a_0^3} r^2 e^{-2r/a_0}$$

**Example: 2**

Find The average value of  $r$  in this 1s orbit and the average potential energy

**Solution:**

The average of  $r$  in the 1s orbit is

$$\langle r \rangle_{1s} = \frac{4}{a_o^3} \int_0^{\infty} r^3 e^{-2r/a_o} dr = \frac{3}{2} a_o$$

And the average potential energy is

$$\begin{aligned} \langle U(r) \rangle_{1s} &= \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \int_0^{\infty} dr r^2 \psi_{1s}^*(r, \theta, \phi) \left[ -\frac{e^2}{4\pi\epsilon_o a_o r} \right] \psi_{1s}(r, \theta, \phi) = -\frac{e^2}{\pi\epsilon_o a_o} \int_0^{\infty} dr r e^{-2r/a_o} \\ &= -\frac{e^2}{4\pi\epsilon_o a_o} \end{aligned}$$

### Virial Theorem

It is interesting to note that from the above example and equation 10 that

$$\langle U(r) \rangle = 2\langle E \rangle \quad (13)$$

And because  $\langle K \rangle + \langle U(r) \rangle = \langle E \rangle$

$$\left. \begin{aligned} \langle U(r) \rangle &= -2\langle K \rangle \\ \text{and} \\ \langle K \rangle &= -\langle E \rangle \end{aligned} \right\} \quad (14)$$

This equation (Eq.14) is called the Virial Theorem and is valid for all atoms and molecules.

Although we have derived this equation for the 1s state of the hydrogen atom, it is generally true for any system in which the potential energy is Coulombic. The virial theorem provides a general equation relating the average over time of the total kinetic energy,  $\langle K \rangle$ , of a stable system consisting of N particles, bound by potential forces, with that of the total potential energy,  $\langle U(r) \rangle$ , where angle brackets represent the average over time of the enclosed quantity.

(The word "virial" derives from vis, the Latin word for "force" or "energy", and was given its technical definition by Rudolf Clausius in 1870)

The next simplest orbital is the 2s orbital and is given by

$$\psi_{2s}(r, \theta, \phi) = R_{20}(r)Y_0^0(\theta, \phi) = \frac{1}{\sqrt{32\pi}} \left(\frac{2}{a_0}\right)^{\frac{3}{2}} \left(2 - \frac{r}{a_0}\right) e^{-\frac{r}{2a_0}} \quad (15)$$

The average value of r in the 2s state is

$$\langle r \rangle_{2s} = \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \int_0^{\infty} dr r^2 \psi_{2s}^*(r, \theta, \phi) \psi_{2s}(r, \theta, \phi) = 6a_0 \quad (16)$$

Showing that

1- Any s orbital will have the angular factor  $Y_0^0(\theta, \phi)$  and so they are generally spherically symmetric

2- The 2s electron is on the average a much greater distance from the nucleus than a 1s electron.

**Question: using the general properties of the associated Laguerre polynomials, Prove that it is possible to write that**

$$\langle r \rangle_{ns} = \frac{3}{2} a_0 n^2 \quad (17)$$

**For the case  $l \neq 0$**

The hydrogen atomic wave functions are not spherically symmetric, they depend on  $\theta$  and  $\phi$ . In this section we shall concentrate on the angular parts of the hydrogen wave functions.

Let us consider the case for  **$l = 1$**  there are three p orbitals for each value of n.  $Y_1^0(\theta, \phi), Y_1^{\pm 1}(\theta, \phi)$ . The simplest of these spherical harmonics is

$$Y_1^0(\theta, \phi) = \left(\frac{3}{4\pi}\right)^{\frac{1}{2}} \cos\theta \quad (18)$$

$$\underline{l = 2}$$

A 3d<sub>0</sub> wave function is given by

$$\psi_{320} = \psi_{3d_0}(r, \theta, \phi) = R_{30}(r)Y_2^0(\theta, \phi) = R_{30}(r) \left(\frac{5}{16\pi}\right)^{\frac{1}{2}} (3\cos^2\theta - 1) \quad (19)$$

And the angular part is represented in the figure 1 below.

The angular functions with  $m \neq 0$  are more difficult to represent pictorially because they not only depend on  $\phi$  in addition to  $\theta$  but complex as well. In particular the state with  $m \neq 0$  are

$$Y_1^{+1}(\theta, \phi) = \left(\frac{3}{8\pi}\right)^{1/2} \sin \theta e^{+i\phi} \quad 20)$$

$$\text{and } Y_1^{-1}(\theta, \phi) = \left(\frac{3}{8\pi}\right)^{1/2} \sin \theta e^{-i\phi} \quad 21)$$

the probability densities associated with both of them is the same

$$|Y_1^{\pm 1}(\theta, \phi)| = \frac{3}{8\pi} \sin^2 \theta \quad 22)$$

## 5-2 spinning

In addition to its orbital magnetic moment, an electron as well as protons, neutrons and other particle has an intrinsic property called spin that also contributes to its magnetic moment.

The magnitude of the angular momentum  $S$  associated with spin is on the same order of magnitude as the magnitude of the angular momentum  $L$  due to the orbital motion of an electron. The magnitude of the **spin angular momentum** of an electron predicted by quantum theory is

$$S = \frac{\sqrt{3}}{2} \hbar \quad 23)$$

And the spin **magnetic moment** is

$$\mu_{spin} = \frac{e\hbar}{2m_e} = 9.27 \times 10^{-24} \text{ J/T}$$

This combination of constants is called Bohr magneton . In atoms containing many electrons, the electrons usually pair up with their spin opposite each other; thus, the spin magnetic moments cancelled . However for the case of atoms containing an odd number of electrons must have some spin magnetic moment.



The total magnetic moment of an electron is the vector sum of the orbital and spin angular moments ( $\mu_B = 9.27 \times 10^{-24} \text{ J/T}$ ,  $\mu_{He} = 0 \text{ J/T}$ ). And  $\hat{L}^2$  The eigenvalue equations for

$$\hat{L}^2 Y_l^m(\theta, \phi) = \hbar^2 l(l+1) Y_l^m(\theta, \phi)$$

And we

$$\hat{L}_z Y_l^m(\theta, \phi) = m \hbar Y_l^m(\theta, \phi)$$

we define the **spin operators**  $\hat{S}^2$  and  $\hat{S}_z$  and their eigenfunctions  $\alpha$  and  $\beta$

by the equations  $l = \frac{1}{2}$

$$\hat{S}^2 \alpha = \frac{1}{2} \left( \frac{1}{2} + 1 \right) \hbar^2 \alpha$$

$$\hat{S}^2 \beta = \frac{1}{2} \left( \frac{1}{2} + 1 \right) \hbar^2 \beta$$

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$$\hat{S}_z \alpha = \frac{1}{2} \hbar \alpha$$

$$\hat{S}_z \beta = \frac{1}{2} \hbar \beta$$

In a sense,  $\alpha = Y_{\frac{1}{2}}^{\frac{1}{2}}$  and  $\beta = Y_{\frac{1}{2}}^{-\frac{1}{2}}$  they are called the spin eigenfunction and they are orthonormal. Also as we can write that the value of the orbital angular momentum of an electron in the hydrogen atom

$$L = \hbar \sqrt{l(l+1)}$$

We can say that the spin angular momentum of an electron is

$$S = \hbar \sqrt{s(s+1)}$$

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Then  $s = \frac{\sqrt{3}}{2} \hbar$  as mentioned before in Eq.23

We must now include the spin function with the spatial wave function and since they are independent we write

$$\Psi(x, y, z, \sigma) = \psi(x, y, z) \alpha(\sigma) \quad \text{or} \quad \Psi(x, y, z, \sigma) = \psi(x, y, z) \beta(\sigma) \quad 26)$$

The complete one electron wave function  $\Psi$  is called a spin orbital. Using the hydrogenlike wave function as example, the first two spin orbital of it is

$$\psi_{100 \frac{1}{2}} = \left( \frac{Z^3}{\pi} \right)^{\frac{1}{2}} e^{-Zr} \alpha$$

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$$\psi_{100-\frac{1}{2}} = \left( \frac{Z^3}{\pi} \right)^{\frac{1}{2}} e^{-Zr} \beta \quad 28)$$

The fourth quantum number is called the spin quantum number  $m_s$  introduced by Pauli which give a good answers to many question arises when placing an atom into magnetic fiel. **Pauli** state the his famous **Exclusion principle** restrict that: **“ no two electrons in an atom can have the same values of all quantum numbers  $n, m, L, m_s$  “**. This principle can be restated to that all electronic wave functions must be antisymmetric under the interchange of any two electrons.

If we take the case of Helium as an example

$$\psi(1,2) = \psi_{100-\frac{1}{2}}(1)\psi_{100-\frac{1}{2}}(2) = 1s\alpha(1)1s\beta(2) \quad 13)$$

And because electrons are indistinguishable from each other and cannot really be labeld

$$\psi(2,1) = \psi_{100-\frac{1}{2}}(2)\psi_{100-\frac{1}{2}}(1) = 1s\alpha(2)1s\beta(1) \quad 14)$$

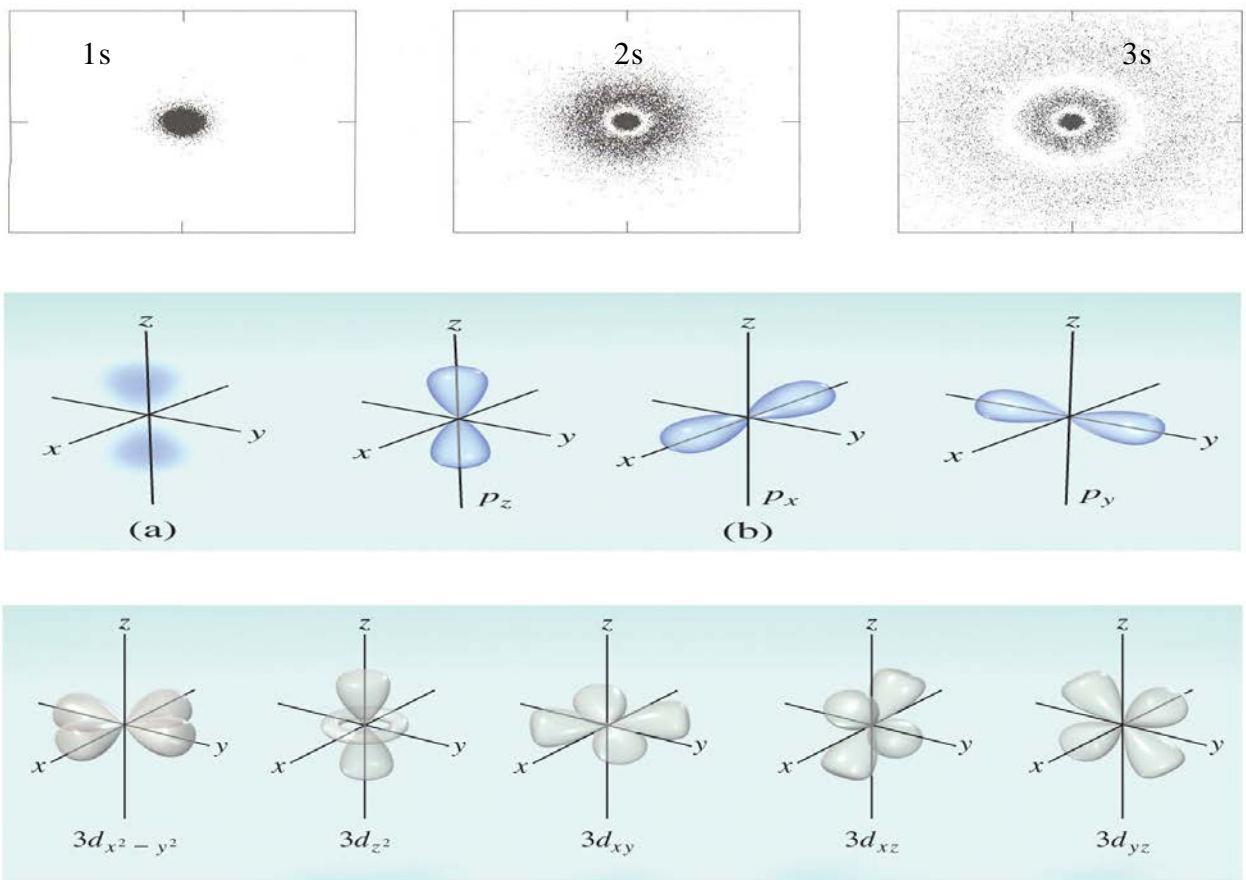


Figure 1