

Chapter 7

The Quantum Theory of the Hydrogen Atom

7.1 Schrödinger's Equation for Hydrogen Atom

The potential energy of the electron-proton system is electrostatic, i.e.

$$E_p = V(r) = -\frac{e^2}{4\pi\epsilon_0 r} \quad (7.1)$$

then Schrödinger's equation becomes

$$\nabla^2 \psi + \frac{2m}{\hbar^2} (E - V) \psi = 0$$

Since $V(r)$ is a function of r , to take advantage of this radial symmetry we transform ψ to spherical coordinates. Schrödinger's equation becomes

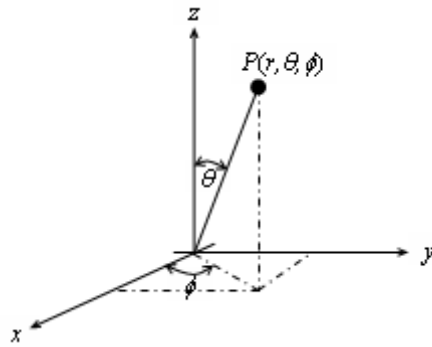


Figure 7.1: Space Quantization

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2m}{\hbar^2} (E - V) \psi = 0 \quad (7.2)$$

§7.2 can be rewritten for finite nuclear mass and hydrogenic atoms by replacing m by m' and e^2 by Ze^2 .

Let us try a solution of the form (*separation of variables*)

$$\psi(r, \theta, \phi) = R(r)f(\theta)g(\phi) \quad (7.3)$$

This substitution allows us to separate the p.d.e. (§7.2) into three separate ordinary differential equations.

$$\frac{\partial \psi}{\partial r} = fg \frac{\partial R}{\partial r}, \quad \frac{\partial \psi}{\partial \theta} = Rg \frac{\partial f}{\partial \theta}, \quad \frac{\partial^2 \psi}{\partial \phi^2} = Rf \frac{\partial^2 g}{\partial \phi^2}, \quad (7.4)$$

Substituting §7.4 into §7.2 and rearranging, we get

$$\frac{\sin^2 \theta}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + \frac{2m}{\hbar^2} r^2 \sin^2 \theta (E - V) + \frac{\sin \theta}{f} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial f}{\partial \theta} \right) = -\frac{1}{g} \frac{\partial^2 g}{\partial \phi^2} \quad (7.5)$$

The left side of the equation cannot change as ϕ changes, since it does not depend on ϕ . Similarly, the right side cannot change with either r or θ . This implies each side of §7.5 should equal to a constant;

$$\boxed{-\frac{1}{g} \frac{\partial^2 g}{\partial \phi^2} = m_l^2} \quad \text{Azimuthal equation} \quad (7.6)$$

Substituting m_l^2 in §7.5 and rearranging,

$$\frac{1}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + \frac{2mr^2}{\hbar^2} (E - V) = \frac{m_l^2}{\sin^2 \theta} - \frac{1}{f \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial f}{\partial \theta} \right) \quad (7.7)$$

Both side of §7.7 should equal a constant- let it be $l(l+1)$

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2m}{\hbar^2} \left(E - V - \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} \right) R = 0 \quad (7.8)$$

- Radial equation

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{df}{d\theta} \right) \left(l(l+1) - \frac{m_l^2}{\sin^2 \theta} \right) f = 0 \quad (7.9)$$

- Angular equation

7.2 Quantum Numbers

The solution to §7.6 is

$$g(\phi) = Ae^{jm_l \phi}$$

since $g(\phi)$ should be single-valued, then

$$\begin{aligned} g(\phi) &= g(\phi + 2\pi) \\ \Rightarrow Ae^{jm_l\phi} &= Ae^{jm_l(\phi+2\pi)} \\ \Rightarrow m_l &= 0, \pm 1, \pm 2, \dots \end{aligned}$$

m_l is called the *magnetic quantum number*.

Solution to §7.7 (the angular equation) is given in terms of *associated Legendre polynomials* that occur in the study of spherical harmonics. Application of boundary conditions result in

$$\begin{aligned} |m_l| &\leq l \\ \text{or } m_l &= 0, \pm 1, \pm 2, \dots, \pm l. \end{aligned}$$

Solutions to §7.8 (the radial equation) are given by the *associate Laguerre polynomial*. The equation is solved only when E is positive or has one of the negative values E_n given by

$$E_n = -\frac{E_o}{n^2} \quad (7.10)$$

where $E_o = \frac{\hbar^2}{2ma_o^2} = 13.6 \text{ eV}$ and $a_o = \frac{4\pi\epsilon_o\hbar^2}{me^2}$ is the Bohr radius! We see that the solution needs another quantum number n . Application of boundary conditions to §7.8 yield

$$0 \leq l < n$$

So we have three quantum numbers associated with §7.5

n - principal (total) quantum number

l - orbital quantum number

m_l - magnetic quantum number.

$$\begin{aligned} n &= 1, 2, 3, \dots \\ l &= 0, 1, 2, \dots, n-1 \\ m_l &= -l, -l+1, \dots, 0, 1, \dots, l-1, l \\ &\quad (0, \pm 1, \pm 2, \dots, \pm l) \end{aligned} \quad (7.11)$$

Finally the wave function of the electron in a hydrogen atom can be written as

$$\psi(r, \theta, \phi) = R_{nl}(r)f_{lm_l}(\theta)g_{m_l}(\phi)$$

Example 7.1: What are the possible quantum numbers for a $n = 4$ state in atomic hydrogen?

7.3 Interpretation of the Quantum Numbers

1. Principal(Total) Quantum Number, n

It results from the solution of the radial wave function $R(r)$ (§7.8). It describes the quantization of electron energy in the hydrogen atom

$$E_n = -\frac{E_o}{n^2} = -\frac{me^4}{8\varepsilon_o^2 h^2} \frac{1}{n^2}$$

2. Orbital Quantum Number, l

It is associated with the $R(r)$ and $f(\theta)$ part of the wave function. The electron-proton system has orbital angular momentum as the particles pass around each other. This angular momentum is

$$\begin{aligned}\mathbf{L} &= \mathbf{r} \times \mathbf{p}, \quad \text{or} \\ L &= m v_{\text{orbital}} r\end{aligned}\tag{7.12}$$

where v_{orbital} is the orbital velocity perpendicular to the radius. The quantum number l is related to L by

$$L = \sqrt{l(l+1)}\hbar\tag{7.13}$$

Note that the quantum result disagrees with the Bohr theory which states that $L = n\hbar$. For example, if $l = 0$ then $L = \sqrt{0(1)}\hbar = 0$.

A certain energy level is said to be *degenerate* with respect to l when the energy is independent of the value of l . For example, the energy for $n = 3$ level is the same for all possible values of l ($l = 0, 1, 2$).

Letters are used for various values of l as

$$\begin{array}{cccccccc} l : & 0 & 1 & 2 & 3 & 4 & 5 & 6 & \dots \\ \text{letter:} & s & p & d & f & g & h & i & \dots \end{array}$$

The first four letters stand for *sharp*, *principal*, *diffuse*, and *fundamental*, respectively. After $l = 3$ (f state), the letters generally follow alphabetical order. Atomic states are referred to by the n number and l letter. For example, a state with $n = 2$ and $l = 1$ is called $2p$ state.

Example 7.2: Determine the principal and orbital quantum numbers for the following states (if allowed) $1s, 2s, 4d, 6g, 2d$.

3. Magnetic Quantum Number, m_l

The angular momentum $\mathbf{L}$ is a vector quantity but l only determines its magnitude. The magnetic quantum number quantizes the component of $\mathbf{L}$ along an external magnetic field, according to the equation

$$L_z = m_l \hbar\tag{7.14}$$

where it is supposed that the external magnetic field is parallel to the z -axis.

Note that m_l arises in the solution of $g(\phi)$.

As an example, consider $l = 2$. Then

$$\begin{aligned} L &= \sqrt{l(l+1)}\hbar = \sqrt{6}\hbar \\ \text{but } m_l &= 0, \pm 1, \pm 2. \\ \therefore L_z &= 0, \pm\hbar, \pm 2\hbar \end{aligned}$$

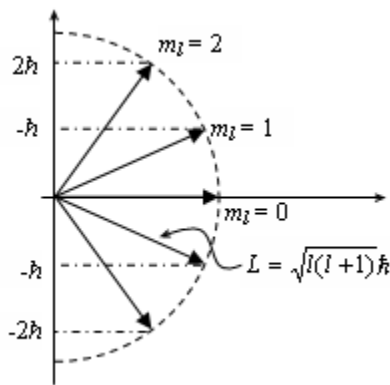


Figure 7.2: Space Quantization

Since only certain orientations of $\mathbf{L}$ are allowed, this phenomenon is called *space quantization*.

7.4 Magnetic Effects on Atomic Spectra- The Normal Zeeman Effect

The wave mechanical description of the hydrogen atom gives an accurate account of its properties. However, shortcomings persist at least in two important respects; first, *fine structure* (called the *anomalous Zeeman effect*) of the spectral lines in the absence of any external magnetic field (it can be resolved by considering the electron's intrinsic spin) and second, their splitting into three lines in the presence of external magnetic field (called the *normal Zeeman effect*). The normal Zeeman effect can be understood by considering the atom to behave like a small magnet.

Consider the electron as a circulating current loop. The current loop has a magnetic moment

$$\begin{aligned} \mu &= IA, \quad \text{current } I = \frac{dq}{dt} = \frac{\text{electron charge}}{\text{period}} \\ \therefore \mu &= IA = \frac{qA}{T} = \frac{(-e)\pi r^2}{2\pi r/v} = -\frac{erv}{2} = -\frac{e}{2m}L \end{aligned} \quad (7.15)$$

where $L = mvr$ is the angular momentum and A is the area enclosed by the electron orbit. μ and L are vectors:

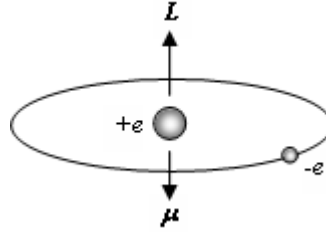


Figure 7.3: Angular momentum and magnetic moment

$$\bar{\mu} = -\frac{e}{2m}\mathbf{L} \quad (7.16)$$

In the absence of external magnetic field, $\bar{\mu}$ of atoms point in random directions. If there is a field $\mathbf{B}$, atoms experience a torque $\bar{\tau} = \bar{\mu} \times \mathbf{B}$ tending to align $\bar{\mu}$ with $\mathbf{B}$, then

$$\mu_z = -\frac{e}{2m}L_z = -\frac{e}{2m}\hbar m_l = -\mu_B m_l \quad (7.17)$$

where $\mu_B = \frac{e}{2m}\hbar$ is a unit of magnetic moment called a *Bohr magneton*.

Potential energy of a magnet in an external field is

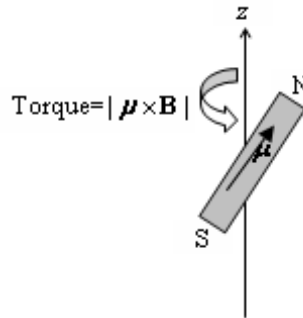


Figure 7.4: Torque

$$V_B = -\bar{\mu} \cdot \mathbf{B} \quad (7.18)$$

with $\mathbf{B}$ along z . The energy of the orbiting electron in a magnetic field is

$$V_B = -\mu_z B = +\mu_B m_l B \quad (7.19)$$

The potential energy is thus quantized according to the magnetic quantum number m_l ; each (degenerate) atomic level of given l is split into $2l + 1$

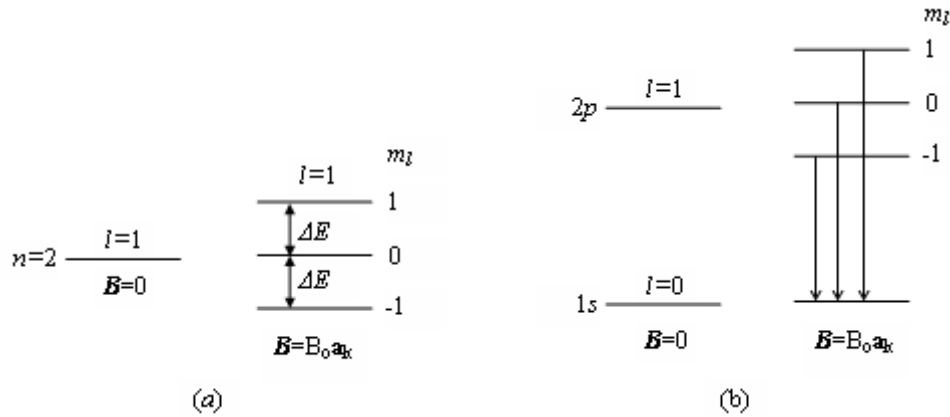


Figure 7.5: The Normal Zeeman Effect

different energy states according to the value of m_l (i.e. the degeneracy is removed).

$$\Delta E = \mu_B B \Delta m_l \quad (7.20)$$

Example 7.3: What is the value of the Bohr magneton? Calculate the energy difference between the $m_l = 0$ and $m_l = +1$ components in the $2p$ state of atomic hydrogen placed in an external field of 2T.

7.5 Intrinsic Spin

The anomalous optical spectra can be explained by assigning a fourth quantum number to the electron - the *spin quantum number*. Due to its spin, an electron has magnetic dipole moment and also an angular momentum independent of its orbital motion.

From experimental data, the intrinsic spin quantum number s is $\frac{1}{2}$. By analogous with the other quantum numbers, there will be $2s+1 = 2(\frac{1}{2})+1 = 2$ components of the spin angular momentum vector $\mathbf{S}$. Thus the *magnetic spin quantum number* m_s has only two values; $m_s = \pm \frac{1}{2}$.

Now, the atomic state can be completely described by four quantum numbers (n, l, m_l, m_s) . These states will be degenerate in energy unless the atom is in a magnetic field. In a magnetic field, these states will have different energies due to an energy separation like that of §7.20. In the absence an external magnetic field, the fourth quantum number, m_s , makes the degeneracy of the n^{th} quantum level $2n^2$.

Example 7.4: How many distinct different states exist for the $5f$ level of atomic

hydrogen?

7.6 Selection Rule

The *transition probabilities* for the electron from one state to the another can be calculated from the solution of the Schrödinger equation. The change is more probable when $\Delta l = \pm 1$ (called *allowed* and if $\Delta \neq \pm 1$, it has almost zero probability (called *forbidden transition*)).

The selection rule be summarized as:

$$\begin{aligned}\Delta n &= \text{can be anything} \\ \Delta l &= \pm 1 \\ \Delta m_l &= 0, \pm 1 \\ m_s &= \text{can (but need not) change between } \frac{1}{2} \text{ and } -\frac{1}{2}\end{aligned}\tag{7.21}$$

From fig.7.6, there are no transitions for $3P \rightarrow 2P$, $3D \rightarrow 2S$ and $3S \rightarrow 1S$

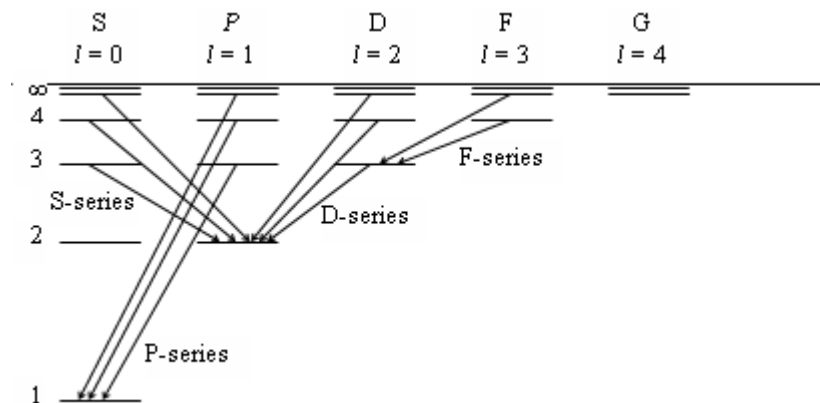


Figure 7.6: Allowed Photon Transitions

because $\Delta l \neq \pm 1$. (Capital letters represent angular momentum)

Example 7.5: Which of the following transitions are allowed for the hydrogen atom, and if allowed, what is the energy involved?

1. $(2, 1, 1, \frac{1}{2}) \rightarrow (4, 2, 1, \frac{1}{2})$
2. $(4, 2, -1, -\frac{1}{2}) \rightarrow (2, 1, 0, \frac{1}{2})$
3. $(5, 2, 1, \frac{1}{2}) \rightarrow (4, 2, 1, -\frac{1}{2})$

7.7 Probability Distribution Function

The azimuthal probability density $g(\phi)g^*(\phi)$ is constant

$$\begin{aligned} g(\phi) &= Ae^{jm_l\phi} \\ \therefore g(\phi)g^*(\phi) &= A^2 \\ \text{but } \int_0^{2\pi} gg^* d\phi &= 1 \\ \Rightarrow A^2 \int_0^{2\pi} d\phi &= 1 \Rightarrow A = \frac{1}{\sqrt{2\pi}} \end{aligned}$$

Therefore, the normalized azimuthal function is

$$g(\phi) = \frac{1}{\sqrt{2\pi}} e^{jm_l\phi}$$

$R(r)$ can be used to calculate the radial probability distribution of the electron. The probability of finding the electron between r and $r + dr$ is

$$\begin{aligned} dP &= \Psi\Psi^* dV \\ \text{but } dV &= r^2 \sin\theta dr d\theta d\phi \\ \therefore dP &= p(r)dr \\ &= r^2 R(r)R^*(r) dr \int_0^\pi |f(\theta)|^2 \sin\theta d\theta \int_0^{2\pi} |g(\phi)|^2 d\phi \end{aligned}$$

Therefore,

$$\boxed{p(r)dr = r^2 |R(r)|^2 dr} \quad (7.22)$$

7.8 Some Wave Functions for Few Quantum Numbers

Similarly, the angular and azimuthal solutions are grouped together to form *spherical harmonics* $Y(\theta, \phi)$, defined as

$$Y(\theta, \phi) = f(\theta)g(\phi)$$

Exercise 7.1: Plot R_{nl} and $P_{nl}(r)$ for $n = 1, 2, 3$.

Exercise 7.2: Plot $f_{lm_l}(\theta)$ for $l = 0, 1, 2$.

Example 7.6: Write down all the wave functions for the $2p$ level of hydrogen atom.

Example 7.7: Find the most probable radius for the electron of a hydrogen atom in the $1s$ and $2p$ states.

Exercise 7.3: For a hydrogen atom in $6f$ state, what is the minimum angle between the orbital angular momentum and the z -axis?

Table 7.1: Hydrogen Atom Radial Wave Function (Laguerre Polynomials)

n	l	$R_{nl}(r)$
1	0	$\frac{2}{a_o^{3/2}} e^{-r/a_o}$
2	0	$\left(2 - \frac{r}{a_o}\right) \frac{e^{-r/2a_o}}{(2a_o)^{3/2}}$
2	1	$\frac{r}{a_o} \frac{e^{-r/2a_o}}{\sqrt{3}(2a_o)^{3/2}}$
3	0	$\frac{1}{(a_o)^{3/2}} \frac{2}{81\sqrt{3}} \left(27 - 18\frac{r}{a_o} + 2\frac{r^2}{a_o^2}\right) e^{-r/3a_o}$
3	1	$\frac{1}{(a_o)^{3/2}} \frac{4}{81\sqrt{6}} \left(6 - 18\frac{r}{a_o}\right) \frac{r}{a_o} e^{-r/3a_o}$
3	2	$\frac{1}{(a_o)^{3/2}} \frac{4}{81\sqrt{30}} \frac{r^2}{a_o^2} e^{-r/3a_o}$

Exercise 7.4: The red Balmer series line in hydrogen ($\lambda = 656.2$ nm) is observed to split into three different spectral lines with $\Delta\lambda = 0.04$ nm between two adjacent lines when placed in a magnetic field B. What is the value of B?

Exercise 7.5: Using all four quantum numbers (n, l, m_l, m_s) write down all possible sets of quantum numbers for the $6d$ state of the hydrogen atom.

Exercise 7.6: Find the most probable radial position for the electron of the hydrogen atom in the $2s$ state.

Exercise 7.7: Find the average radial position for the electron of the hydrogen atom in the $2s$ and $2p$ states.

Exercise 7.8: Calculate the probability of an electron in the $2s$ state of the hydrogen atom being inside the region of the proton (diameter $\approx 2 \times 10^{-15}$ m). Repeat for $2p$ electron. (Hint $r \ll a$)

Table 7.2: Spherical Harmonics

l	m_l	Y_{lm_l}
0	0	$\frac{1}{2\sqrt{\pi}}$
1	0	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$
1	± 1	$\mp\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta e^{\pm j\phi}$
2	0	$\frac{1}{4}\sqrt{\frac{5}{\pi}}(3\cos^2\theta - 1)$
2	± 1	$\mp\frac{1}{2}\sqrt{\frac{15}{2\pi}}\sin\theta\cos\theta e^{\pm j\phi}$
2	± 1	$\frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2\theta e^{\pm 2j\phi}$