Chapter 6.   The Hydrogen Atom

Notes:
- *Most of the material in this chapter is taken from Thornton and Rex, Chapter 7.*

6.1 The Schrödinger Equation of the Hydrogen Atom

We now apply the time-independent Schrödinger equation to solve the hydrogen atom. That is, we will endeavour to determine its wave functions and other important parameters related to them, e.g., their energy and angular momentum. This is an important problem not only because hydrogen is the most abundant and fundamental atom in the universe, but also because it can be solved exactly. The solution thus obtained can then be compared to experiments, as well as with the earlier atomic model of Bohr.

A few aspects of the problem first need to be established and dealt with before we can proceed and analyse it. Perhaps the most important concerns the potential energy of the system. This energy is the one that defines the interaction between the nucleus (i.e., the proton) and the electron, and is therefore electrostatic in nature

$$V(r) = -\frac{e^2}{4\pi\varepsilon_0 r}, \tag{6.1}$$

with r the distance between the two particles. The Schrödinger equation also contains a term for the kinetic energy of the system, defined as the square of the momentum divided by twice the mass. One question that arises at this point concerns the identification of this mass; what should it be? We saw in Problem 3 of the Second Assignment the correct equation for the values of r *within the context of the Bohr atomic model* are obtained when the *reduced mass* is used

$$\mu = \frac{m_e M_n}{M_n + m_e} \tag{6.2}$$

instead of the electron mass, with m_e and M_n are the masses of the electron and nucleus, respectively. Although we will not formerly proof this here, the same applies for the Schrödinger model of the hydrogen atom; we must use the reduced mass.

While we have so far only dealt with one-dimensional problems (e.g., the particle in a box and the barrier potential), it is the case that the problem we are now facing is three-dimensional. We should therefore resort to using not only the Cartesian x coordinate, for example, but all three such variables (x,y,z). Although the problem could in principle be solved using Cartesian coordinates, the spherical symmetry of the hydrogen atom does not lend itself well to such approach. Indeed, Cartesians coordinates are perfectly adapted to problems of rectangular symmetries (e.g., a "two-" or three-dimensional box) but are poorly suited to spherically symmetric configurations. This symmetry of the hydrogen atom is set by the electrostatic potential of equation (6.1), which only depends on the
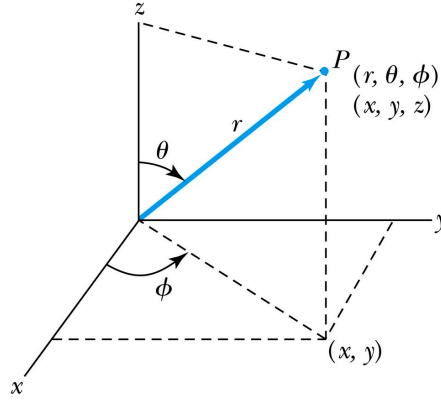
Figure 1 – Relationship between the spherical and Cartesian sets coordinates.

distance between the proton and electron. Since using Cartesian coordinates would thus unnecessarily complicate the solution of the problem, we adopt the so-called *spherical coordinates* (r,θ,ϕ) defined through (see Figure 1)

$$x = r\sin(\theta)\cos(\phi)$$
$$y = r\sin(\theta)\sin(\phi) \quad\quad\quad (6.3)$$
$$z = r\cos(\theta),$$

or

$$r = \sqrt{x^2 + y^2 + z^2}$$
$$\theta = \cos^{-1}\left(\frac{z}{r}\right)$$
$$= \tan^{-1}\left(\frac{\sqrt{x^2 + y^2}}{z}\right) \quad\quad\quad (6.4)$$
$$\phi = \tan^{-1}\left(\frac{y}{x}\right).$$

The variables θ and ϕ are the *polar* and *azimuthal angles*, respectively. Accounting for equations (6.1) to (6.4) we can write the Schrödinger equation as

$$E\psi(r,\theta,\phi) = \left[-\frac{\hbar^2}{2\mu}\nabla^2 + V(r)\right]\psi(r,\theta,\phi). \quad\quad\quad (6.5)$$

The last thing for us to do then is to also write the expression for the Laplacian ∇^2 using spherical coordinates. Formally, we need to transform the Cartesian coordinates version

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{6.6}$$

to its spherical coordinates equivalent with equations (6.3). A derivation of how this is done is beyond the scope of our analysis, and we will simply insert the corresponding transformation in the Schrödinger equation

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin(\theta)}\frac{\partial}{\partial\theta}\left[\sin(\theta)\frac{\partial\psi}{\partial\theta}\right] + \frac{1}{r^2\sin^2(\theta)}\frac{\partial^2\psi}{\partial\phi^2} + \frac{2\mu}{\hbar^2}\left[E - V(r)\right]\psi = 0, \tag{6.7}$$

where it is understood that $\psi = \psi(r,\theta,\phi)$.

As we did when we solved the time-dependent Schrödinger equation for the case of a conservative system, we will now assume that the wave function can be separated into a product of three functions, one for each variable. That is, we write

$$\psi(r,\theta,\phi) = R(r)f(\theta)g(\phi). \tag{6.8}$$

Insertion of this relation in equation (6.7), and dividing by $\psi(r,\theta,\phi)$ yields the following second-order differential equation

$$-\frac{\sin^2(\theta)}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2\mu}{\hbar^2}r^2\sin^2(\theta)\left[E - V(r)\right] - \frac{\sin(\theta)}{f}\frac{d}{d\theta}\left[\sin(\theta)\frac{df}{d\theta}\right] = \frac{1}{g}\frac{d^2g}{d\phi^2}. \tag{6.9}$$

We note that the left-hand side of this equation is a function of r and θ, while the right-hand side only involves ϕ. For the same reasons evoked when separating the time-dependent Schrödinger equation into a product of a spatial and a temporal equation, we can write

$$\frac{1}{g}\frac{d^2g}{d\phi^2} = -m^2, \tag{6.10}$$

with m a constant (please note that it is not a mass). It is straightforward to verify that equation (6.10) allows as solution

$$g_m(\phi) \propto e^{jm\phi}. \tag{6.11}$$

By inserting equation (6.10) on the right-hand side of (6.9) we find that we can further separate its left-hand side to

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2\mu r^2}{\hbar^2}\left[E-V(r)\right]=\frac{m^2}{\sin^2(\theta)}-\frac{1}{f\sin(\theta)}\frac{d}{d\theta}\left[\sin(\theta)\frac{df}{d\theta}\right] \quad (6.12)$$

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

with ℓ yet a new constant. We are then left with the following two differential equations to solve

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

$$\frac{1}{\sin(\theta)}\frac{d}{d\theta}\left[\sin(\theta)\frac{df}{d\theta}\right]+\left[\ell(\ell+1)-\frac{m^2}{\sin^2(\theta)}\right]f=0. \quad (6.13)$$

Although we will not solve these differential equations, we can gain some insight by looking more closely at the radial equation in the simplest case when $\ell=0$. The first of equations (6.13) then becomes

$$\frac{d^2R}{dr^2}+\frac{2}{r}\frac{dR}{dr}+\frac{2\mu}{\hbar^2}\left(E+\frac{e^2}{4\pi\varepsilon_0 r}\right)R=0, \quad (6.14)$$

where we used equation (6.1) for the potential energy. It can easily be verified that equation (6.14) allows solutions of the type

$$R(r)=Ae^{-r/a_0}, \quad (6.15)$$

with A and a_0 some constants. Inserting equation (6.15) into (6.14) yields

$$\left(\frac{1}{a_0^2}+\frac{2\mu}{\hbar^2}E\right)+\left(\frac{2\mu e^2}{4\pi\varepsilon_0\hbar^2}-\frac{2}{a_0^2}\right)\frac{1}{r}=0, \quad (6.16)$$

which in order to be verified for all values of r requires that

$$a_0=\frac{4\pi\varepsilon_0\hbar^2}{\mu e^2} \quad (6.17)$$

$$=5.29\times10^{-11}\mathrm{m}$$

and

$$E=-\frac{\hbar^2}{2\mu a_0^2} \quad (6.18)$$

$$=-E_0.$$

Table 7.1 Hydrogen Atom Radial Wave Functions

n	ℓ	$R_{n\ell}(r)$
1	0	$\dfrac{2}{(a_0)^{3/2}}\,e^{-r/a_0}$
2	0	$\left(2-\dfrac{r}{a_0}\right)\dfrac{e^{-r/2a_0}}{(2a_0)^{3/2}}$
2	1	$\dfrac{r}{a_0}\dfrac{e^{-r/2a_0}}{\sqrt{3}(2a_0)^{3/2}}$
3	0	$\dfrac{1}{(a_0)^{3/2}}\dfrac{2}{81\sqrt{3}}\left(27-18\dfrac{r}{a_0}+2\dfrac{r^2}{a_0^{\,2}}\right)e^{-r/3a_0}$
3	1	$\dfrac{1}{(a_0)^{3/2}}\dfrac{4}{81\sqrt{6}}\left(6-\dfrac{r}{a_0}\right)\dfrac{r}{a_0}e^{-r/3a_0}$
3	2	$\dfrac{1}{(a_0)^{3/2}}\dfrac{4}{81\sqrt{30}}\dfrac{r^2}{a_0^{\,2}}e^{-r/3a_0}$

It is therefore very rewarding to see that we recover the same relations for the Bohr radius and energy as we derived when dealing with the more primitive model of Bohr. It can also be shown that the full solution to the first of equations (6.13) admits a family of functions that are characterized through the introduction of a quantum number $n = 1, 2, 3, \ldots$ in addition to ℓ such that the exponent of the radial function scales with na_0 and the energy as $E_n = -E_0/n^2$. *Note that both n and ℓ are integers*. These results are once again in agreement with Bohr's model. The first few radial solutions $R_{n\ell}(r)$ for a small range of values for n and ℓ are shown in Table 7.1 above. We note the further restriction $0 \le \ell \le n-1$.

The second of equations (6.13) can also be solved to yield a family functions of the polar angle θ, which are denoted by $f_{\ell m}(\theta)$ from their further dependency on the two quantum numbers ℓ and m. These functions are usually combined with the azimuthal solutions $g_m(\phi)$ given in equation (6.11) to yield the so-called *spherical harmonics*

$$Y_{\ell m}(\theta,\phi) = f_{\ell m}(\theta)g_m(\phi). \tag{6.19}$$

The first few spherical harmonics for a small range of values for ℓ and m are shown in Table 7.2 below. We note the further restriction $|m| \le \ell$, which implies that m can be *either a negative or positive integer*.

We therefore summarise the solutions of the Schrödinger equation for the hydrogen atom with the following family of normalized wave functions

Table 7.2 Normalized Spherical Harmonics $Y(\theta, \phi)$

ℓ	m_ℓ	$Y_{\ell m_\ell}$
0	0	$\dfrac{1}{2\sqrt{\pi}}$
1	0	$\dfrac{1}{2}\sqrt{\dfrac{3}{\pi}}\cos\theta$
1	± 1	$\mp\dfrac{1}{2}\sqrt{\dfrac{3}{2\pi}}\sin\theta\, e^{\pm i\phi}$
2	0	$\dfrac{1}{4}\sqrt{\dfrac{5}{\pi}}(3\cos^2\theta - 1)$
2	± 1	$\mp\dfrac{1}{2}\sqrt{\dfrac{15}{2\pi}}\sin\theta\cos\theta\, e^{\pm i\phi}$
2	± 2	$\dfrac{1}{4}\sqrt{\dfrac{15}{2\pi}}\sin^2\theta\, e^{\pm 2i\phi}$
3	0	$\dfrac{1}{4}\sqrt{\dfrac{7}{\pi}}(5\cos^3\theta - 3\cos\theta)$
3	± 1	$\mp\dfrac{1}{8}\sqrt{\dfrac{21}{\pi}}\sin\theta(5\cos^2\theta - 1)\, e^{\pm i\phi}$
3	± 2	$\dfrac{1}{4}\sqrt{\dfrac{105}{2\pi}}\sin^2\theta\cos\theta\, e^{\pm 2i\phi}$
3	± 3	$\mp\dfrac{1}{8}\sqrt{\dfrac{35}{\pi}}\sin^3\theta\, e^{\pm 3i\phi}$

$$\psi_{n\ell m}(r,\theta,\phi) = R_{n\ell}(r)Y_{\ell m}(\theta,\phi), \qquad (6.20)$$

where it is understood that the three quantum numbers verify $n = 1, 2, 3, \ldots$, $0 \le \ell \le n-1$, and $|m| \le \ell$, which we will soon discuss in more details.

We also note that both the radial functions and spherical harmonics are independently normalized. But we must be careful in considering the normalization process. This is because as we move from Cartesian to spherical coordinates we must make the following substitution in the normalization integral

$$dx\, dy\, dz = r^2 \sin(\theta)\, dr\, d\theta\, d\phi, \qquad (6.21)$$

and therefore

$$\int_0^{2\pi} \int_0^{\pi} \int_0^{\infty} |\psi_{n\ell m}(r,\theta,\phi)|^2 \, r^2 \sin(\theta) \, dr \, d\theta \, d\phi = 1. \tag{6.22}$$

This can alternatively be written as

$$\int_0^{\infty} |R_{n\ell}(r)|^2 \, r^2 \, dr = 1$$
$$\int_0^{2\pi} \int_0^{\pi} |Y_{\ell m}(\theta,\phi)|^2 \sin(\theta) \, d\theta \, d\phi = 1. \tag{6.23}$$

The energy of the atom, not subjected to an external field, in a given stationary state $\psi_{n\ell m}$ is solely determined by the *principal quantum number* n through

$$E_n = -\frac{\mu}{2} \left(\frac{e^2}{4\pi\varepsilon_0 \hbar} \right)^2 \frac{1}{n^2}$$
$$= -\frac{E_0}{n^2}. \tag{6.24}$$

The lowest-energy stationary state $n = 1$ is called the *ground state*, for which $E_0 = 13.6 \text{ eV}$, while those corresponding to greater values of the principal quantum number are *excited states*.

The quantum number ℓ is called the *orbital angular quantum number*. We refer to the first of equations (6.13) to understand why it is defined this way. That is, let us write

$$K_{\text{rot}} = \frac{\ell(\ell+1)\hbar^2}{2\mu r^2}, \tag{6.25}$$

which we know has units of energy. Because we also know that the Planck constant $\hbar$ has units of angular momentum, it is tempting to define

$$L = \sqrt{\ell(\ell+1)}\hbar \tag{6.26}$$

for the magnitude of the orbital angular momentum of the atom and relate equation (6.25) to its kinetic energy of rotation

$$K_{\text{rot}} = \frac{L^2}{2I}, \tag{6.27}$$

where $I = \mu r^2$ is the moment of inertia associated with the atom. Although the expression for the magnitude of the orbital angular momentum may appear a little strange by the presence of $\sqrt{\ell(\ell+1)}$ instead of ℓ, we note that it is consistent with Bohr's

correspondence principle since $\ell^2 \simeq \ell(\ell+1)$ for large values of ℓ. With this understanding of the meaning for quantum numbers n and ℓ we find the surprising result that *the ground state of the hydrogen atom has no orbital angular momentum*. This result is at odds with the prediction of the Bohr model. The same can be said for any state when $\ell = 0$. Finally, the letters 's', 'p', 'd', 'd', 'g', etc., are usually associated with values of '0', '1', '2', '3', '4', etc. for ℓ. The energy-orbital angular momentum states are therefore denoted by 1s, 2s, 2p, 3s, 3p, 3d, etc.

Let us now consider the z component of the angular momentum operator

$$
\begin{aligned}
\hat{L}_z &= \left[\mathbf{r} \times \hat{\mathbf{p}} \right]_z \\
&= x\hat{p}_y - y\hat{p}_x \\
&= -j\hbar \left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} \right).
\end{aligned}
\tag{6.28}
$$

We can use the chain rule to write

$$
\begin{aligned}
\frac{\partial}{\partial x} &= \frac{\partial r}{\partial x}\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial x}\frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial x}\frac{\partial}{\partial \phi} \\
\frac{\partial}{\partial y} &= \frac{\partial r}{\partial y}\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial y}\frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial y}\frac{\partial}{\partial \phi},
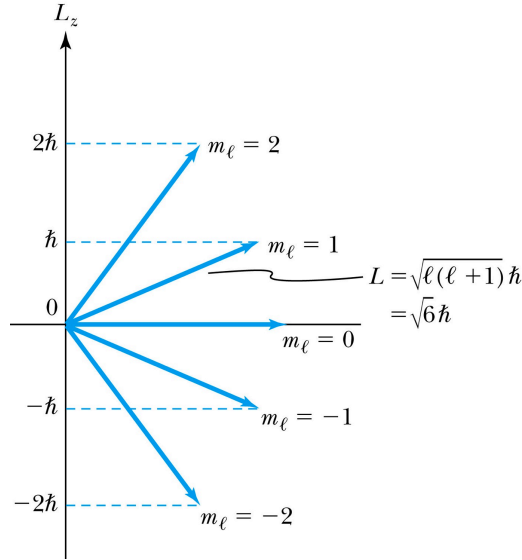\end{aligned}
\tag{6.29}
$$

and

$$
x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} = \left(x\frac{\partial r}{\partial y} - y\frac{\partial r}{\partial x} \right)\frac{\partial}{\partial r} + \left(x\frac{\partial \theta}{\partial y} - y\frac{\partial \theta}{\partial x} \right)\frac{\partial}{\partial \theta} + \left(x\frac{\partial \phi}{\partial y} - y\frac{\partial \phi}{\partial x} \right)\frac{\partial}{\partial \phi}.
\tag{6.30}
$$

Using equations (6.4) to calculate the needed derivatives we find that the first two terms within parentheses on the right-hand side of equation (6.30) equal zero and

$$
\begin{aligned}
x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} &= \left(1+\frac{y^2}{x^2} \right)\left[\frac{d}{d(y/x)}\tan^{-1}\left(\frac{y}{x} \right) \right]\frac{\partial}{\partial \phi} \\
&= \left(1+\frac{y^2}{x^2} \right)\left[\frac{1}{1+(y/x)^2} \right]\frac{\partial}{\partial \phi} \\
&= \frac{\partial}{\partial \phi},
\end{aligned}
\tag{6.31}
$$

which yields

Figure 2 – Representation of orbital angular momentum vector operator for $\ell = 2$.

$$\hat{L}_z = -j\hbar \frac{\partial}{\partial \phi}. \tag{6.32}$$

Referring to equations (6.11), (6.19), and (6.20) we then find the important result that

$$\hat{L}_z \psi_{n\ell m}(r,\theta,\phi) = m\hbar \psi_{n\ell m}(r,\theta,\phi). \tag{6.33}$$

The quantum number m is therefore to be associated with the component of the orbital momentum directed along the z-axis. A representation for this is shown in Figure 2 for $\ell = 2$. Note that $\left|\hat{L}_z\right| < L = \sqrt{\ell(\ell+1)}\hbar$ always, and therefore the operator $\hat{\mathbf{L}}$ can never be directed along $\hat{L}_z$. We note that the choice of the z-axis for this quantum number is entirely arbitrary, any of the other two axes would evidently work just as well. It is important to realize, however, that only one axis can be quantized. For example, if we know ℓ and m, then we also know precisely the values for L and $\left|\hat{L}_z\right|$. The additional knowledge of, say, $\left|\hat{L}_x\right|$ would then further yield an equally precise determination of $\left|\hat{L}_y\right| = \sqrt{L^2 - \hat{L}_x^2 - \hat{L}_z^2}$. This is equivalent to confining the motion of the electron to a plane, which would then imply that its linear momentum in a direction perpendicular to that plane (i.e., along $\hat{\mathbf{L}}$) would be exactly zero. This is, of course, forbidden by the Heisenberg inequality $\Delta r_i \Delta p_i \geq \hbar/2$, with i specifying the x-, y-, or z-axis; *only one component of the orbital angular momentum can be quantized.*

The quantum number m is referred to as the *magnetic quantum number*. This is because the z-axis will usually be chosen to be aligned with an external magnetic field, when one

is present, since as can be shown, the orbital angular momentum operator $\hat{\mathbf{L}}$, which is parallel to the magnetic moment of the atom (see Exercise 4 below), will precess about the magnetic field. The axis defined by the magnetic field is therefore a natural choice for the quantization of $\hat{L}_z$.

Exercises

1. Although we did explain the origin of the orbital angular momentum quantum number ℓ, we have not justified the choice for $\ell(\ell+1)$ instead of, say, ℓ^2 when separating the Schrödinger equation for the hydrogen atom. Show that the mean value of the square of the orbital angular momentum can be evaluated with $\langle L^2 \rangle = 3\langle L_z^2 \rangle$ and the choice of $\ell(\ell+1)$ follows naturally from the fact that $-\ell \leq m \leq \ell$.

Solution.

Since there is nothing special about the choice of the x-, y-, and z-axis, i.e., different people may orient them differently, the average values of the corresponding orbital angular momentum components must be equal $\langle L_x^2 \rangle = \langle L_y^2 \rangle = \langle L_z^2 \rangle$. We therefore have

$$\begin{aligned} \langle L^2 \rangle &= \langle L_x^2 \rangle + \langle L_y^2 \rangle + \langle L_z^2 \rangle \\ &= 3\langle L_z^2 \rangle. \end{aligned} \tag{6.34}$$

We now calculate

$$\begin{aligned} \langle L_z^2 \rangle &= \frac{1}{2\ell+1} \sum_{m=-\ell}^{\ell} (m\hbar)^2 \\ &= \frac{\hbar^2}{2\ell+1} 2 \sum_{m=1}^{\ell} m^2 \\ &= \frac{\hbar^2}{2\ell+1} 2 \left[\frac{\ell(\ell+1)(2\ell+1)}{6} \right] \\ &= \frac{\ell(\ell+1)}{3}, \end{aligned} \tag{6.35}$$

where we have used the identity $\sum_{m=1}^{\ell} m^2 = \ell(\ell+1)(2\ell+1)/6$. It follows from equations (6.34) and (6.35) that

$$\langle L^2 \rangle = \ell(\ell+1)\hbar^2. \tag{6.36}$$

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

Solution.

For the 1s state we have (note the "r^2" term)

$$P_{10}(r) = r^2 |R_{10}(r)|^2$$
$$= \frac{4r^2}{a_0^3} e^{-2r/a_0},$$

(6.37)

and the most probable radius is determined by solving $dP_{10}(r)/dr = 0$. We then write

$$\frac{dP_{10}(r)}{dr} = \frac{4}{a_0^3} \left(2r - \frac{2r^2}{a_0} \right) e^{-2r/a_0}$$
$$= 0,$$

(6.38)

or $r = a_0$.

For the 2p state $P_{21}(r) = r^4/(24a_0^5) e^{-r/a_0}$ and

$$\frac{dP_{21}(r)}{dr} = \frac{1}{24a_0^5} \left(4r^3 - \frac{r^4}{a_0} \right) e^{-r/a_0}$$
$$= 0,$$

(6.39)

or $r = 4a_0$.

3. Calculate the average orbital radius of a 1s electron in the hydrogen atom.

Solution.

The average radius for that state is given by

$$\langle r \rangle = \int_0^\infty R_{10}^*(r) r R_{10}(r) r^2 \, dr$$
$$= \frac{4}{a_0^3} \int_0^\infty r^3 e^{-2r/a_0} \, dr,$$

(6.40)

which is solved by successively integrating by parts three times to obtain

$$\langle r \rangle = \frac{4}{a_0^3} \cdot \frac{3a_0^4}{8}$$

$$= \frac{3}{2} a_0.$$

(6.41)

4. The magnetic moment $\boldsymbol{\mu}$ associated with a current loop of current I has a magnitude equal to IA, where A is the area contained within the loop, and is oriented along the axis perpendicular to the plane of the loop in a direction consistent with the *right-hand rule*.

(a) Use classical physics to show that the magnetic moment of an electron tracing a simple circular current loop is

$$\boldsymbol{\mu} = -\frac{e}{2m_e} \mathbf{L}.$$

(6.42)

(b) Show that equation (6.42) is also valid in quantum mechanics for the hydrogen atom by considering the component $\hat{\mu}_z$, if we replace the electron mass by the reduced mass. Also, show that the expected value of this magnetic moment operator is

$$\langle \mu_z \rangle = -\frac{m_e}{\mu} \mu_B m,$$

(6.43)

with m the magnetic quantum number and the *Bohr magneton*

$$\mu_B = \frac{e\hbar}{2m_e}.$$

(6.44)

Solution.

(a) We consider an electron of charge $-e$ going around on a circle of radius r at speed v and, for simplicity, we set the loop in the xy-plane with the centre of the circle at the origin. Using the definition for the magnetic moment we write

$$\mu_z = -\underbrace{\frac{ev}{2\pi r}}_{I} \cdot \underbrace{\pi r^2}_{A}$$

$$= -\frac{e}{2m_e} \cdot m_e vr$$

(6.45)

$$= -\frac{e}{2m_e} L_z.$$

Since the current loop could be oriented in any manner we may choose this equation can be generalize vectorially as follows

$$\boldsymbol{\mu} = -\frac{e}{2m_e}\mathbf{L}. \tag{6.46}$$

(b) For the quantum mechanical hydrogen atom's magnetic moment component $\hat{\mu}_z$, we should consider the azimuthal velocity operator $\hat{v}_\phi$ and its corresponding orbital radius $r\sin(\theta)$. The quantum mechanical magnetic moment operator is therefore

$$\hat{\mu}_z = -\underbrace{\frac{e\hat{v}_\phi}{2\pi r\sin(\theta)}}_{I}\cdot\underbrace{\pi r^2\sin^2(\theta)}_{A}$$

$$= -\frac{e}{2\mu}\cdot\mu\hat{v}_\phi r\sin(\theta) \tag{6.47}$$

$$= -\frac{e}{2\mu}\hat{L}_z.$$

However, we can use equation (6.32) to transform equation (6.47) to

$$\hat{\mu}_z = j\frac{e\hbar}{2\mu}\frac{\partial}{\partial\phi}$$

$$= j\frac{m_e}{\mu}\mu_B\frac{\partial}{\partial\phi}. \tag{6.48}$$

The expected value of this magnetic moment operator is calculated using equation (6.22)

$$\langle\hat{\mu}_z\rangle = \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty}R_{n\ell}^*(r)Y_{\ell m}^*(\theta,\phi)\hat{\mu}_z R_{n\ell}(r)Y_{\ell m}(\theta,\phi)r^2\sin(\theta)dr\,d\theta\,d\phi$$

$$= j\frac{m_e}{\mu}\mu_B\int_0^{\infty}R_{n\ell}^*(r)r^2R_{n\ell}(r)dr\cdot\int_0^{2\pi}\int_0^{\pi}Y_{\ell m}^*(\theta,\phi)\frac{\partial}{\partial\phi}Y_{\ell m}(\theta,\phi)\sin(\theta)d\theta\,d\phi \tag{6.49}$$

but using equations (6.23) and

$$\frac{\partial}{\partial\phi}Y_{\ell m}(\theta,\phi) = jmY_{\ell m}(\theta,\phi) \tag{6.50}$$

we finally get

$$\langle\hat{\mu}_z\rangle = j\frac{m_e}{\mu}\mu_B\cdot jm\int_0^{2\pi}\int_0^{\pi}\left|Y_{\ell m}(\theta,\phi)\right|^2\sin(\theta)d\theta\,d\phi$$

$$= -\frac{m_e}{\mu}\mu_B m. \tag{6.51}$$

6.2 The Electron Intrinsic Angular Momentum or Spin

As we will see in the Third Assignment, an external magnetic field will interact with the magnetic moment of the hydrogen atom (or any atom or molecule, for that matter). This interaction adds a small amount to the energy level E_n of a stationary state $\psi_{n\ell m}$ (see equation (6.24)) that is proportional to the magnetic quantum number m. This means that the energy levels are not solely dependent on n anymore, but also on m and the external magnetic field strength. For example, the energy levels for a np state (i.e., $\ell = 1$) will be unchanged at E_n for the $m = 0$ state, while it will increase by $\mu_B B$ for $m = 1$ and decrease by the same amount for $m = -1$ (B is the magnetic field strength). Although these energy changes are small, they were easily measurable well before modern quantum mechanics was developed. They would manifest themselves through the appearance of spectral lines at the corresponding energies (frequencies $\nu_n = E_n/h$); this is the co-called *normal Zeeman effect*.

It soon became clear, however, that the spectra measured for different atoms subjected to an external magnetic field where more complicated than predicted by the normal Zeeman effect. In particular, it was realized from an experiment by **Samuel Goudsmit** (1902-1978) and **George Uhlenbeck** (1900-1988) that another magnetic moment component was needed beyond that due to the orbital angular momentum to explain their result. It was, in fact, Goudsmit and Uhlenbeck who proposed that the electron must possess an *intrinsic magnetic moment*, which would presumably result from an *intrinsic angular momentum* called *spin*. Although it is tempting to associate this intrinsic angular momentum with a rotation of the electron about "an axis going through its centre," this interpretation quickly runs into troubles and the spin is known to be a purely quantum mechanical phenomenon. In particular, it is found that the spin operator $\hat{\mathbf{S}}$ is, not unlike the orbital angular momentum $\hat{\mathbf{L}}$, characterized by an *intrinsic spin quantum number* $s = 1/2$ and a *magnetic spin quantum number* $m_s = \pm 1/2$. It is commonly said that the spin is pointing *up* when $m_s = 1/2$ and *down* if $m_s = -1/2$. These new quantum numbers play the same roles as ℓ and m, respectively, but it is very important to note that *in the case of the electron they are half-integers*. As a result we have the following relation for the magnitude of the electron spin operator $S = \left|\hat{\mathbf{S}}\right| = \sqrt{s(s+1)}\,\hbar = \sqrt{3/4}\,\hbar$. Furthermore, if we define the magnetic moment associated to the orbital angular momentum of an electron with (see Exercise 4 above)

$$\hat{\boldsymbol{\mu}}_\ell = -\frac{g_\ell \mu_B}{\hbar}\hat{\mathbf{L}}, \tag{6.52}$$

where $g_\ell = 1$, then magnetic moment due to the intrinsic spin is

$$\hat{\boldsymbol{\mu}}_s = -\frac{g_s \mu_B}{\hbar}\hat{\mathbf{S}}, \tag{6.53}$$

with $g_s = 2$. The constants g_ℓ and g_s are *gyromagnetic ratios*.

The intrinsic spin is a most important characteristic of all fundamental particles. In fact, particles are divided in two overarching families depending on the type of spin they possess. Particles that have a half-integer spin, such as the electron with $s = 1/2$, are called *fermions*, while the others that have integer spin (including zero), like the photon with $s = 1$, are called *bosons*. This differentiation is very important as the two groups follow completely different statistics; fermions follows the *Fermi-Dirac distribution* and the bosons the *Bose-Einstein distribution*. We also note that non-fundamental particles can also have a spin, e.g., the proton has a $s = 1/2$ spin.