Chapter 2

The Hydrogen atom

In the previous chapter we gave a quick overview of the Bohr model, which is only really valid in the semiclassical limit. (cf. section 1.7.) We now begin our task in earnest by applying quantum mechanics to the simplest atom we know, namely the hydrogen atom.

It is well known from classical physics that planetary orbits are characterized by their energy and angular momentum. In this chapter we apply the Schrödinger equation to the hydrogen atom to find the allowed energies and angular momenta of the nucleus-electron system. In classical systems we are also able to calculate the precise trajectory of the orbit. This is not possible in quantum systems. The best we shall be able to do is to find the wave functions. These will then give us the probability amplitudes that allow us to calculate all the measurable properties of the system.

2.1 The Schrödinger Equation

The time-independent Schrödinger equation for hydrogen is given by:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} \right) \, \Psi(r,\theta,\phi) = E \, \Psi(r,\theta,\phi) \,. \tag{2.1}$$

This is written in terms of the spherical polar co-ordinates (r, θ, ϕ) because atoms are spheres, and the use of spherical polar co-ordinates simplifies the solutions. Note that we are considering the motion of the electron relative to a stationary nucleus here. As with all two-body problems, this means that the mass that enters into the equation is the **reduced mass** defined previously in eqn 1.9:

$$\frac{1}{m} = \frac{1}{m_{\rm e}} + \frac{1}{m_{\rm N}} \,. \tag{2.2}$$

For hydrogen where $m_{\rm N} = m_{\rm p}$, the reduced mass is very close to m_e, and has a value of $0.9995 m_e$.

Written out explicitly, we have

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial r} \right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Psi}{\partial\theta} \right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\Psi}{\partial\phi^2} \right] - \frac{Ze^2}{4\pi\epsilon_0 r} \, \Psi = E \, \Psi \tag{2.3}$$

Our task is to find the wave functions $\Psi(r,\theta,\phi)$ that satisfy this equation, and hence to find the allowed quantized energies E.

2.2 Angular momentum

The classical definition of angular momentum is:

$$\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p} \,. \tag{2.4}$$

For circular orbits this simplifies to $L = mvr$, and in Bohr's model, L was quantized in integer units of $\hbar$. (See eqn 1.7.) However, the full quantum treatment is more complicated, and requires the introduction of two other quantum numbers l and m_l, as we shall now see.

The components of $\boldsymbol{L}$ are given by

$$\begin{pmatrix} L_x \\ L_y \\ L_z \end{pmatrix} = \begin{pmatrix} x \\ y \\ z \end{pmatrix} \times \begin{pmatrix} p_x \\ p_y \\ p_z \end{pmatrix} = \begin{pmatrix} yp_z - zp_y \\ zp_x - xp_z \\ xp_y - yp_x \end{pmatrix} \,. \tag{2.5}$$

In quantum mechanics we represent the linear momentum by differential operators of the type

$$\hat{p}_x = -i\hbar \frac{\partial}{\partial x} . \tag{2.6}$$

Therefore, the quantum mechanical operators for the angular momentum are given by:

$$\hat{L}_x = \frac{\hbar}{i} \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \tag{2.7}$$

$$\hat{L}_y = \frac{\hbar}{i} \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \tag{2.8}$$

$$\hat{L}_z = \frac{\hbar}{i} \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) . \tag{2.9}$$

Note that the "hat" symbol indicates that we are representing an operator and not just a number.

The magnitude of the angular momentum is given by:

$$L^2 = L_x^2 + L_y^2 + L_z^2 .$$

We therefore define the quantum mechanical operator $\hat{\boldsymbol{L}}^2$ by

$$\hat{\boldsymbol{L}}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 . \tag{2.10}$$

Note that operators like $\hat{L}_x^2$ should be understood in terms of repeated operations:

$$\hat{L}_x^2 \psi = -\hbar^2 \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \left(y \frac{\partial \psi}{\partial z} - z \frac{\partial \psi}{\partial y} \right)$$

$$= -\hbar^2 \left(y^2 \frac{\partial^2 \psi}{\partial z^2} - y \frac{\partial \psi}{\partial y} - z \frac{\partial \psi}{\partial z} - 2yz \frac{\partial^2 \psi}{\partial y \partial z} + z^2 \frac{\partial^2 \psi}{\partial y^2} \right) .$$

It can be shown that the components of the angular momentum operator do not commute, that is

$$\hat{L}_x \hat{L}_y \neq \hat{L}_y \hat{L}_x .$$

In fact we can show that:

$$[\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z , \tag{2.11}$$

where the "commutator bracket" $[\hat{L}_x, \hat{L}_y]$ is defined by

$$[\hat{L}_x, \hat{L}_y] = \hat{L}_x \hat{L}_y - \hat{L}_y \hat{L}_x . \tag{2.12}$$

The other commutators of the angular momentum operators, namely $[\hat{L}_y, \hat{L}_z]$ and $[\hat{L}_z, \hat{L}_x]$ are obtained by cyclic permutation of the indices in Eq. 2.11: $x \to y$, $y \to z$, $z \to x$.

This rather esoteric point has deep significance. If two quantum mechanical operators do not commute, then it is not possible to know their values simultaneously. Consider, for example, the operators for position and momentum in a one-dimensional system:

$$[\hat{x}, \hat{p}]\psi = (\hat{x}\hat{p} - \hat{p}\hat{x})\psi = -i\hbar x \left(\frac{d\psi}{dx} \right) + i\hbar \frac{d(x\psi)}{dx} = i\hbar \psi .$$

Thus we have:

$$[\hat{x}, \hat{p}] = i\hbar \neq 0 . \tag{2.13}$$

The fact that $[\hat{x}, \hat{p}] \neq 0$ means that the operators do not commute. This is intrinsically linked to the fact that we cannot measure precise values for the position and momentum simultaneously, which we know from the Heisenberg uncertainty principle. The argument based on commutators is thus a more formal way of understanding uncertainty products.

In the case of the angular momentum operators, the fact that $\hat{L}_x$, $\hat{L}_y$ and $\hat{L}_z$ do not commute means that we can only know *one* of the components of $\hat{\boldsymbol{L}}$ at any time. If we know the value of L_z, we cannot know L_x and L_y as well. However, we *can* know the length of the angular momentum vector, because we can show that $\hat{L}^2$ and $\hat{L}_z$ commute. In summary:
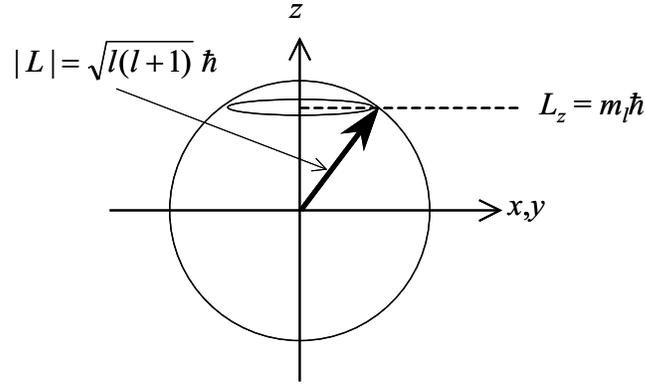
Figure 2.1: Vector model of the angular momentum in an atom. The angular momentum is represented by a vector of length $\sqrt{l(l+1)}\hbar$ precessing around the z-axis so that the z-component is equal to $m_l\hbar$.

- We can know the length of the angular momentum vector L and one of its components.

- For mathematical convenience, we usually take the component we know to be the z component, ie L_z.

- We cannot know the values of all three components of the angular momentum simultaneously.

This is represented pictorially in the **vector model** of the atom shown in figure 2.1. In this model the angular momentum is represented as a vector of length $\sqrt{l(l+1)}\hbar$ precessing around the z axis so that the component along that axis is equal to $m_l\hbar$. The x and y components of the angular momentum are not known.

In spherical polar co-ordinates, the two key angular momentum operators are given by:

$$\hat{L}_z = \frac{\hbar}{i}\frac{\partial}{\partial\phi} \tag{2.14}$$

and

$$\hat{L}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]. \tag{2.15}$$

It is easy to see that the Schrödinger equation given in Eq. 2.3 can be re-written as follows:

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial r}\right) + \frac{\hat{L}^2}{2mr^2}\Psi - \frac{Ze^2}{4\pi\epsilon_0 r}\Psi = E\,\Psi. \tag{2.16}$$

The eigenfunctions of the angular momentum operator are found by solving the equation:

$$\hat{L}^2 F(\theta,\phi) \equiv -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]F(\theta,\phi) = CF(\theta,\phi). \tag{2.17}$$

For reasons that will become clearer later, the constant C is usually written in the form:

$$C = l(l+1)\hbar^2. \tag{2.18}$$

At this stage, l can take any value, real or complex. We can separate the variables by writing:

$$F(\theta,\phi) = \Theta(\theta)\Phi(\phi). \tag{2.19}$$

On substitution into eqn 2.17 and cancelling the common factor of $\hbar^2$, we find:

$$-\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)\Phi - \frac{1}{\sin^2\theta}\Theta\frac{d^2\Phi}{d\phi^2} = l(l+1)\Theta\Phi. \tag{2.20}$$

Multiply by $-\sin^2\theta/\Theta\Phi$ and re-arrange to obtain:

$$\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \sin^2\theta\,l(l+1) = -\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}. \tag{2.21}$$

The left hand side is a function of θ only, while the right hand side is a function of ϕ only. The equation must hold for all values of the θ and ϕ and hence both sides must be equal to a constant. On writing this arbitrary separation constant m^2, we then find:[1]

$$\sin\theta \frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta \frac{\mathrm{d}\Theta}{\mathrm{d}\theta}\right) + l(l+1)\sin^2\theta\,\Theta = m^2\Theta, \tag{2.22}$$

and

$$\frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2} = -m^2\Phi. \tag{2.23}$$

The equation in ϕ is easily solved to obtain:

$$\Phi(\phi) = A\mathrm{e}^{\mathrm{i}m\phi}. \tag{2.24}$$

The wave function must have a single value for each value of ϕ, and hence we require:

$$\Phi(\phi + 2\pi) = \Phi(\phi), \tag{2.25}$$

which requires that the separation constant m must be an integer. Using this fact in eqn 2.22, we then have to solve

$$\sin\theta \frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta \frac{\mathrm{d}\Theta}{\mathrm{d}\theta}\right) + [l(l+1)\sin^2\theta - m^2]\,\Theta = 0, \tag{2.26}$$

with the constraint that m must be an integer. On making the substitution $u = \cos\theta$ and writing $\Theta(\theta) = P(u)$, eqn 2.26 becomes:

$$\frac{\mathrm{d}}{\mathrm{d}u}\left((1-u^2)\frac{\mathrm{d}P}{\mathrm{d}u}\right) + \left[l(l+1) - \frac{m^2}{1-u^2}\right]P = 0. \tag{2.27}$$

Equation 2.27 is known as either the Legendre equation or the associated Legendre equation, depending on whether m is zero or not. Solutions only exist if l is an integer $\geq |m|$ and $P(u)$ is a polynomial function of u. This means that the solutions to eqn 2.26 are of the form:

$$\Theta(\theta) = P_l^m(\cos\theta), \tag{2.28}$$

where $P_l^m(\cos\theta)$ is a polynomial function in $\cos\theta$ called the (associated) **Legendre polynomial** function.
   Putting this all together, we then find:

$$F(\theta,\phi) = \text{normalization constant} \times P_l^m(\cos\theta)\,\mathrm{e}^{\mathrm{i}m\phi}, \tag{2.29}$$

where m and l are integers, and m can have values from $-l$ to $+l$. The correctly normalized functions are called the **spherical harmonic** functions $Y_{l,m}(\theta,\phi)$.
   It is apparent from eqns 2.17 and 2.18 that the spherical harmonics satisfy:

$$\hat{\boldsymbol{L}}^2 Y_{l,m}(\theta,\phi) = l(l+1)\hbar^2 Y_{l,m}(\theta,\phi). \tag{2.30}$$

Furthermore, on substituting from eqn 2.14, it is also apparent that

$$\hat{L}_z Y_{l,m}(\theta,\phi) = m\hbar Y_{l,m}(\theta,\phi). \tag{2.31}$$

The integers l and m that appear here are called the orbital and magnetic quantum numbers respectively. Some of the spherical harmonic functions are listed in Table 2.1. Equations 2.30–2.31 show that the magnitude of the angular momentum and its z-component are equal to $\sqrt{l(l+1)}\hbar$ and $m\hbar$ respectively, as consistent with Fig. 2.1.
   The spherical harmonics have the property that:

$$\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi} Y_{l,m}^*(\theta,\phi)Y_{l',m'}(\theta,\phi)\,\sin\theta\,\mathrm{d}\theta\mathrm{d}\phi = \delta_{l,l'}\delta_{m,m'}. \tag{2.32}$$

The symbol $\delta_{k,k'}$ is called the **Kronecker delta function**. It has the value of 1 if $k = k'$ and 0 if $k \neq k'$. The $\sin\theta$ factor in Eq. 2.32 comes from the volume increment in spherical polar co-ordinates: see Eq. 2.47 below.

---

[1]Be careful not to confuse the magnetic quantum number m with the reduced mass that has the same symbol! Note also that a subscript l is often added (i.e. m_l) to distinguish it from the quantum number for the z-component of the spin (m_s).

l	m	$Y_{l,m}(\theta,\phi)$
0	0	$\sqrt{\frac{1}{4\pi}}$
1	0	$\sqrt{\frac{3}{4\pi}}\cos\theta$
1	± 1	$\mp\sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm i\phi}$
2	0	$\sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1)$
2	± 1	$\mp\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{\pm i\phi}$
2	± 2	$\sqrt{\frac{15}{32\pi}}\sin^2\theta e^{\pm 2i\phi}$

Table 2.1: Spherical harmonic functions.

2.3 Separation of variables in the Schrödinger equation

The Coulomb potential is an example of a **central field**. This means that the force only lies along the radial direction. This allows us separate the motion into the radial and angular parts. Hence we write:

$$\Psi(r,\theta,\phi) = R(r)\,Y(\theta,\phi)\,. \tag{2.33}$$

On substituting this into Eq. 2.16, we find

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}R}{\mathrm{d}r}\right)Y + R\frac{\hat{\boldsymbol{L}}^2 Y}{2mr^2} - \frac{Ze^2}{4\pi\epsilon_0 r}RY = E\,RY\,. \tag{2.34}$$

Multiply by r^2/RY and re-arrange to obtain:

$$-\frac{\hbar^2}{2m}\frac{1}{R}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}R}{\mathrm{d}r}\right) - \frac{Ze^2 r}{4\pi\epsilon_0} - Er^2 = -\frac{1}{Y}\frac{\hat{\boldsymbol{L}}^2 Y}{2m}\,. \tag{2.35}$$

The left hand side is a function of r only, while the right hand side is only a function of the angular co-ordinates θ and ϕ. The only way this can be true is if both sides are equal to a constant. Let's call this constant $-\hbar^2\ell(\ell+1)/2m$, where ℓ is an arbitrary number at this stage. This gives us, after a bit of re-arrangement:

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}R(r)}{\mathrm{d}r}\right) + \frac{\hbar^2\ell(\ell+1)}{2mr^2}R(r) - \frac{Ze^2}{4\pi\epsilon_0 r}R(r) = ER(r)\,, \tag{2.36}$$

and

$$\hat{\boldsymbol{L}}^2 Y(\theta,\phi) = \hbar^2\ell(\ell+1)Y(\theta,\phi)\,. \tag{2.37}$$

On comparing Eqs. 2.30 and 2.37 we can now identify the arbitrary separation constant ℓ with the angular momentum quantum number l, and we can see that the function $Y(\theta,\phi)$ that enters Eq. 2.37 must be one of the spherical harmonics.

We can tidy up the radial equation Eq. 2.36 by writing:

$$R(r) = \frac{P(r)}{r}\,.$$

This gives:

$$\left[-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{\hbar^2 l(l+1)}{2mr^2} - \frac{Ze^2}{4\pi\epsilon_0 r}\right]P(r) = EP(r)\,. \tag{2.38}$$

This now makes physical sense. It is a Schrödinger equation of the form:

$$\hat{H}P(r) = EP(r)\,, \tag{2.39}$$
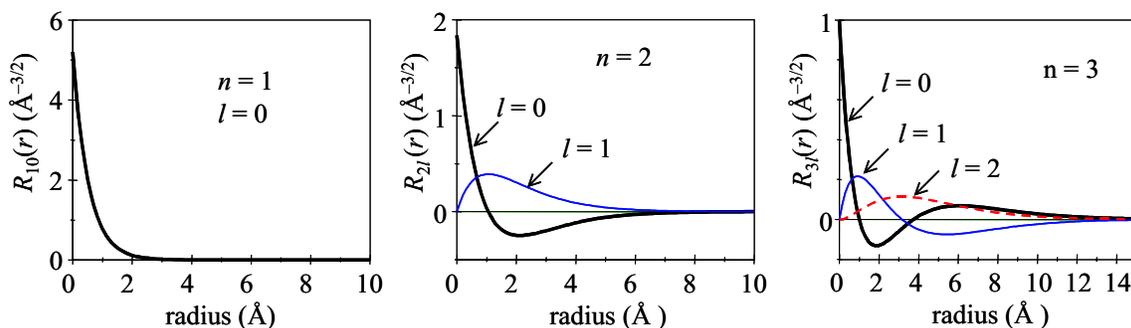
Figure 2.2: The radial wave functions $R_{nl}(r)$ for the hydrogen atom with $Z = 1$. Note that the axes for the three graphs are not the same.

where the energy operator $\hat{H}$ (i.e. the Hamiltonian) is given by:

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}r^2} + V_{\text{effective}}(r)\,. \tag{2.40}$$

The first term in eqn 2.40 is the **radial kinetic energy** given by

$$\text{K.E.}_{\text{radial}} = \frac{p_r^2}{2m} = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}r^2}\,.$$

The second term is the **effective potential energy**:

$$V_{\text{effective}}(r) = \frac{\hbar^2 l(l+1)}{2mr^2} - \frac{Ze^2}{4\pi\epsilon_0 r}\,, \tag{2.41}$$

which has two components. The first of these is the orbital kinetic energy given by:

$$\text{K.E.}_{\text{orbital}} = \frac{L^2}{2I} = \frac{\hbar^2 l(l+1)}{2mr^2}\,,$$

where $I \equiv mr^2$ is the moment of inertia. The second is the usual potential energy due to the Coulomb energy.

   This analysis shows that the quantized orbital motion adds quantized kinetic energy to the radial motion. For $l > 0$ the orbital kinetic energy will always be larger than the Coulomb energy at small r, and so the effective potential energy will be positive. This has the effect of keeping the electron away from the nucleus, and explains why states with $l > 0$ have nodes at the origin (see below).

2.4   The wave functions and energies

The wave function we require is given by Eq. 2.33. We have seen above that the $Y(\theta, \phi)$ function that appears in Eq. 2.33 must be one of the spherical harmonics, some of which are listed in Table 2.1. The radial wave function $R(r)$ can be found by solving the radial differential equation given in Eq. 2.36. The mathematics is somewhat complicated and is considered in Section 2.5. Here we just quote the main results.

   Solutions are only found if we introduce an integer quantum number n. The energy depends only on n, but the functional form of $R(r)$ depends on both n and l, and so we must write the radial wave function as $R_{nl}(r)$. A list of some of the radial functions is given in Table 2.2. Representative wave functions are plotted in Fig. 2.2.

   We can now write the full wave function as:

$$\Psi_{nlm}(r, \theta, \phi) = R_{nl}(r)Y_{lm}(\theta, \phi)\,. \tag{2.42}$$

The quantum numbers must obey the following rules:

- n can have any integer value ≥ 1.

- l can have integer values up to $(n - 1)$.

n	l	$R_{nl}(r)$
1	0	$(Z/a_0)^{\frac{3}{2}} 2 \exp(-Zr/a_0)$
2	0	$(Z/2a_0)^{\frac{3}{2}} 2 \left(1 - \frac{Zr}{2a_0}\right) \exp(-Zr/2a_0)$
2	1	$(Z/2a_0)^{\frac{3}{2}} \frac{2}{\sqrt{3}} \left(\frac{Zr}{2a_0}\right) \exp(-Zr/2a_0)$
3	0	$(Z/3a_0)^{\frac{3}{2}} 2 \left[1 - (2Zr/3a_0) + \frac{2}{3}\left(\frac{Zr}{3a_0}\right)^2\right] \exp(-Zr/3a_0)$
3	1	$(Z/3a_0)^{\frac{3}{2}} (4\sqrt{2}/3) \left(\frac{Zr}{3a_0}\right) \left(1 - \frac{1}{2}\frac{Zr}{3a_0}\right) \exp(-Zr/3a_0)$
3	2	$(Z/3a_0)^{\frac{3}{2}} (2\sqrt{2}/3\sqrt{5}) \left(\frac{Zr}{3a_0}\right)^2 \exp(-Zr/3a_0)$

Table 2.2: Radial wave functions of the hydrogen atom. a_0 is the Bohr radius (5.29×10^{-11} m). The wave functions are normalized so that $\int_{r=0}^{\infty} R_{nl}^* R_{nl} r^2 dr = 1$.
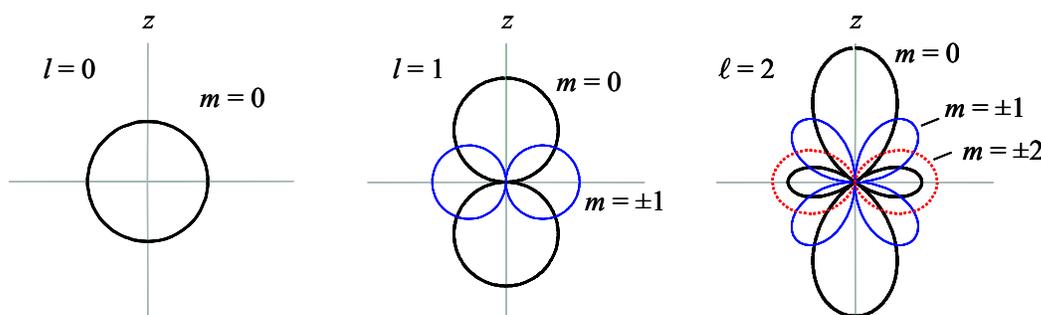
Figure 2.3: Polar plots of the spherical harmonics with $l \leq 2$. The plots are to be imagined with spherical symmetry about the z axis. In these polar plots, the value of the function for a given angle θ is plotted as the distance from the origin. Prettier pictures may be found, for example, at: `http://mathworld.wolfram.com/SphericalHarmonic.html`.

- m can have integer values from $-l$ to $+l$.

These rules drop out of the mathematical solutions. Functions that do not obey these rules will not satisfy the Schrödinger equation for the hydrogen atom.

The radial wave functions listed in Table 2.2 are of the form:

$$R_{nl}(r) = C_{nl} \cdot (\text{polynomial in } r) \cdot e^{-r/a} , \tag{2.43}$$

where $a = na_H/Z$, a_H being the Bohr radius of Hydrogen, namely 5.29×10^{-11} m. C_{nl} is a normalization constant. The polynomial functions that drop out of the equations are polynomials of order $n - 1$, and have $n - 1$ nodes. If $l = 0$, all the nodes occur at finite r, but if $l > 0$, one of the nodes is at $r = 0$.

The angular part of the wave function is of the form (see eqn 2.29 and Table 2.1):

$$Y_{l,m}(\theta, \phi) = C'_{lm} \cdot P_l^m(\cos\theta) \cdot e^{im\phi} , \tag{2.44}$$

where $P_l^m(\cos\theta)$ is a Legendre polynomial, e.g. $P_1^1(\cos\theta) = \text{constant}$, $P_1^0(\cos\theta) = \cos\theta$, etc. C'_{lm} is another normalization constant. Representative polar wave functions are shown in figure 2.3.

The energy of the system is found to be:

$$E_n = -\frac{mZ^2e^4}{8\epsilon_0^2 h^2} \frac{1}{n^2} , \tag{2.45}$$

which is the same as the Bohr formula given in Eq. 1.10. Note that this depends only on the principal quantum number n: all the l states for a given value of n are **degenerate** (i.e. have the same energy),

even though the radial wave functions depend on both n and l. This degeneracy with respect to l is called "accidental", and is a consequence of the fact that the electrostatic energy has a precise $1/r$ dependence in hydrogen. In more complex atoms, the electrostatic energy will depart from a pure $1/r$ dependence due to the shielding effect of inner electrons. In this case, the gross energy depends on l as well as n, even before we start thinking of higher order fine structure effects. We shall see how this works in more detail when we consider the alkali atoms later.

The wave functions are nomalized so that

$$\int_{r=0}^{\infty} \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} \Psi_{n,l,m}^* \Psi_{n',l'm'} \, \mathrm{d}V = \delta_{n,n'}\delta_{l,l'}\delta_{m,m'} \tag{2.46}$$

where $\mathrm{d}V$ is the incremental volume element in spherical polar co-ordinates:

$$\mathrm{d}V = r^2 \sin\theta \, \mathrm{d}r \mathrm{d}\theta \mathrm{d}\phi \,. \tag{2.47}$$

The radial probability function $P_{nl}(r)$ is the probability that the electron is found between r and $r + \mathrm{d}r$:

$$
\begin{aligned}
P_{nl}(r)\,\mathrm{d}r &= \int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi} \Psi^*\Psi \; r^2 \sin\theta \mathrm{d}r\mathrm{d}\theta\mathrm{d}\phi \\
&= |R_{nl}(r)|^2 \, r^2 \, \mathrm{d}r \,.
\end{aligned}
\tag{2.48}
$$

The factor of r^2 that appears here is just related to the surface area of the radial shell of radius r (i.e. $4\pi r^2$.) Some representative radial probability functions are sketched in Fig. 2.4. 3-D plots of the shapes of the atomic orbitals are available at: `http://www.shef.ac.uk/chemistry/orbitron/`.

Expectation values of measurable quantities are calculated as follows:

$$\langle A \rangle = \int\int\int \Psi^* A \Psi \, \mathrm{d}V \,. \tag{2.49}$$

Thus, for example, the expectation value of the radius is given by:

$$
\begin{aligned}
\langle r \rangle &= \int\int\int \Psi^* r \Psi \mathrm{d}V \\
&= \int_{r=0}^{\infty} R_{nl}^* r R_{nl} r^2 \mathrm{d}r \int_{\theta=0}^{\pi} \sin\theta\mathrm{d}\theta \int_{\phi=0}^{2\pi} \mathrm{d}\phi \\
&= \int_{r=0}^{\infty} R_{nl}^* r R_{nl} r^2 \mathrm{d}r \,.
\end{aligned}
\tag{2.50}
$$

This gives:

$$\langle r \rangle = \frac{n^2 a_{\mathrm{H}}}{Z}\left(\frac{3}{2} - \frac{l(l+1)}{2n^2}\right) \,. \tag{2.51}$$

Note that this only approaches the Bohr value, namely $n^2 a_{\mathrm{H}}/Z$ (see eqn 1.15), for the states with $l = n-1$ at large n.

Reading

Demtröder, W., *Atoms, Molecules and Photons*, §4.3 – §5.1.
Haken, H. and Wolf, H.C., *The Physics of Atoms and Quanta*, chapter 10.
Phillips, A.C., *Introduction to Quantum Mechanics*, chapters 8 & 9.
Beisser, A., *Concepts of Modern Physics*, chapter 6.
Eisberg, R. and Resnick, R., *Quantum Physics*, chapter 7.
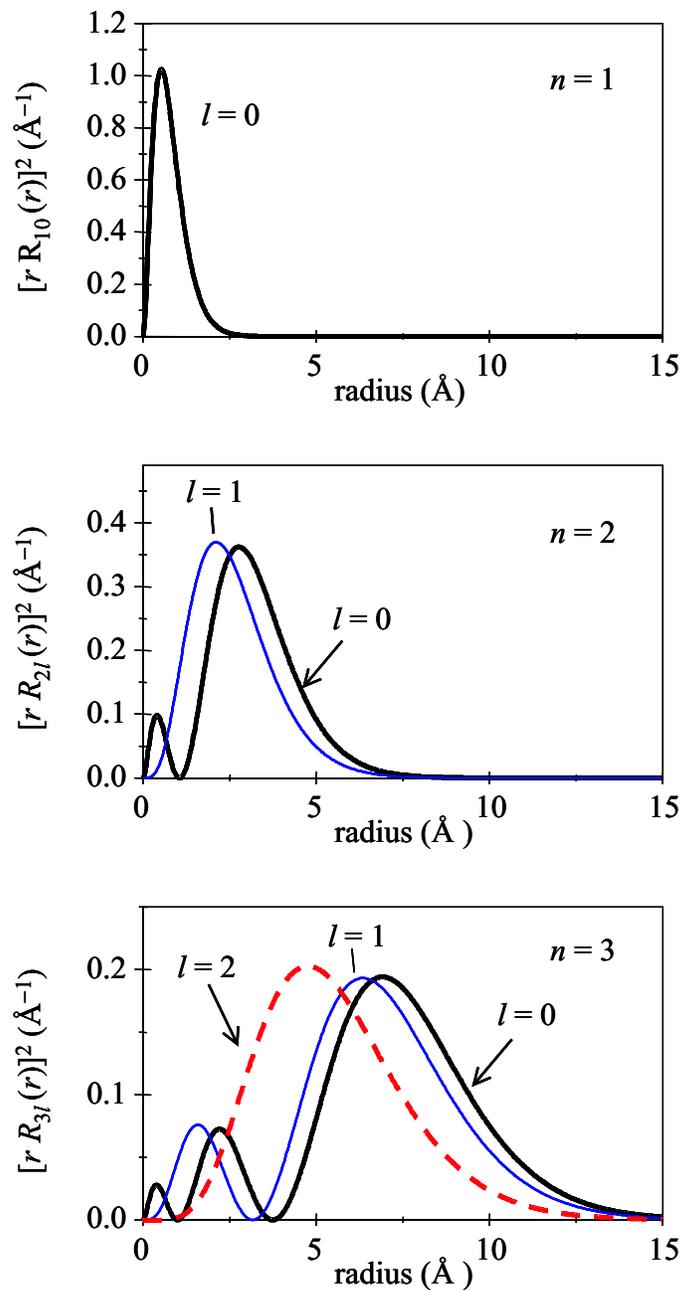
Figure 2.4: Radial probability functions for the first three n states of the hydrogen atom with $Z = 1$. Note that the radial probability is equal to $r^2|R_{nl}(r)|^2$, not just to $|R_{nl}(r)|^2$. Note also that the horizontal axes are the same for all three graphs, but not the vertical axes.

2.5   Appendix: Mathematical solution of the radial equation

The radial wave equation for hydrogen is given from eqn 2.36 as:

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}R(r)}{\mathrm{d}r}\right) + \frac{\hbar^2 l(l+1)}{2mr^2}R(r) - \frac{Ze^2}{4\pi\epsilon_0 r}R(r) = ER(r)\,, \tag{2.52}$$

where l is an integer ≥ 0. We first put this in a more user-friendly form by introducing the dimensionless radius ρ according to:

$$\rho = \left(\frac{8m|E|}{\hbar^2}\right)^{1/2} r\,. \tag{2.53}$$

The modulus sign around E is important here because we are seeking bound solutions where E is negative. The radial equation now becomes:

$$\frac{\mathrm{d}^2 R}{\mathrm{d}\rho^2} + \frac{2}{\rho}\frac{\mathrm{d}R}{\mathrm{d}\rho} - \left(\frac{l(l+1)}{\rho^2} + \frac{\lambda}{\rho} - \frac{1}{4}\right)R = 0\,, \tag{2.54}$$

where

$$\lambda = \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{\hbar}\left(\frac{m}{2|E|}\right)^{1/2}\,. \tag{2.55}$$

We first consider the behaviour at $\rho \to \infty$, where eqn 2.54 reduces to:

$$\frac{\mathrm{d}^2 R}{\mathrm{d}\rho^2} - \frac{1}{4}R = 0\,. \tag{2.56}$$

This has solutions of $\mathrm{e}^{\pm\rho/2}$. The $\mathrm{e}^{+\rho/2}$ solution cannot be normalized and is thus excluded, which implies that $R(\rho) \sim \mathrm{e}^{-\rho/2}$.

Now consider the bahaviour for $\rho \to 0$, where the dominant terms in eqn 2.54 are:

$$\frac{\mathrm{d}^2 R}{\mathrm{d}\rho^2} + \frac{2}{\rho}\frac{\mathrm{d}R}{\mathrm{d}\rho} - \frac{l(l+1)}{\rho^2}R = 0\,, \tag{2.57}$$

with solutions $R(\rho) = \rho^l$ or $R(\rho) = \rho^{-(l+1)}$. The latter diverges at the origin and is thus unacceptable.

The consideration of the asymptotic behaviours suggests that we should look for general solutions of the radial equation with $R(\rho)$ in the form:

$$R(\rho) = L(\rho)\,\rho^l\,\mathrm{e}^{-\rho/2}\,. \tag{2.58}$$

On substituting into eqn 2.54 we find:

$$\frac{\mathrm{d}^2 L}{\mathrm{d}\rho^2} + \left(\frac{2l+2}{\rho} - 1\right)\frac{\mathrm{d}L}{\mathrm{d}\rho} + \frac{\lambda - l - 1}{\rho}L = 0\,. \tag{2.59}$$

We now look for a series solution of the form:

$$L(\rho) = \sum_{k=0}^{\infty} a_k\rho^k\,. \tag{2.60}$$

Substitution into eqn 2.59 yields:

$$\sum_{k=0}^{\infty}\left[k(k-1)a_k\rho^{k-2} + \left(\frac{2l+2}{\rho} - 1\right)ka_k\rho^{k-1} + \frac{\lambda - l - 1}{\rho}a_k\rho^k\right] = 0\,, \tag{2.61}$$

which can be re-written:

$$\sum_{k=0}^{\infty}\left[(k(k-1) + 2k(l+1))a_k\rho^{k-2} + (\lambda - l - 1 - k)a_k\rho^{k-1}\right] = 0\,, \tag{2.62}$$

or alternatively:

$$\sum_{k=0}^{\infty}\left[((k+1)k + 2(k+1)(l+1))a_{k+1}\rho^{k-1} + (\lambda - l - 1 - k)a_k\rho^{k-1}\right] = 0\,. \tag{2.63}$$

This will be satisfied if

$$((k+1)k + 2(k+1)(l+1))a_{k+1} + (\lambda - l - 1 - k)a_k = 0,\qquad(2.64)$$

which implies:

$$\frac{a_{k+1}}{a_k} = \frac{-\lambda + l + 1 + k}{(k+1)(k+2l+2)}.\qquad(2.65)$$

At large k we have:

$$\frac{a_{k+1}}{a_k} \sim \frac{1}{k}.\qquad(2.66)$$

Now the series expansion of e^ρ is

$$e^\rho = 1 + \rho + \frac{\rho^2}{2!} + \cdots \frac{\rho^k}{k!} + \cdots,\qquad(2.67)$$

which has the same limit for a_{k+1}/a_k. With $R(\rho)$ given by eqn 2.58, we would then have a dependence of $e^{+\rho} \cdot e^{-\rho/2} = e^{+\rho/2}$, which is unacceptable. We therefore conclude that the series expansion must terminate for some value of k. Let n_r be the value of k for which the series terminates. It then follows that $a_{n_r+1} = 0$, which implies:

$$-\lambda + l + 1 + n_r = 0,\qquad n_r \geq 0,\qquad(2.68)$$

or

$$\lambda = l + 1 + n_r.\qquad(2.69)$$

We now introduce the **principal quantum number** n according to:

$$n = n_r + l + 1.\qquad(2.70)$$

It follows that:

1. n is an integer,

2. $n \geq l + 1$,

3. $\lambda = n$.

The first two points establish the general rules for the quantum numbers n and l. The third one fixes the energy. On inserting $\lambda = n$ into eqn 2.55 and remembering that E is negative, we find:

$$E_n = -\frac{me^4}{(4\pi\epsilon_0)^2 2\hbar^2} \frac{Z^2}{n^2}.\qquad(2.71)$$

This is the usual Bohr result. The wave functions are of the form given in eqn 2.58:

$$R(\rho) = \rho^l\, L(\rho)\, e^{-\rho/2}.\qquad(2.72)$$

The polynomial series $L(\rho)$ that satisfies eqn 2.59 is known as an **associated Laguerre function**. On substituting for ρ from eqn 2.53 with $|E|$ given by eqn 2.71, we then obtain:

$$R(r) = \text{normalization constant} \times \text{Laguerre polynomial in } r \times r^l e^{-r/a}\qquad(2.73)$$

as before (cf. eqn 2.43), with

$$a = \left(\frac{\hbar^2}{2m|E|}\right)^{1/2} = \frac{4\pi\epsilon_0 \hbar^2}{me^2} \frac{n}{Z} \equiv \frac{n}{Z} a_H,\qquad(2.74)$$

where a_H is the Bohr radius of hydrogen.