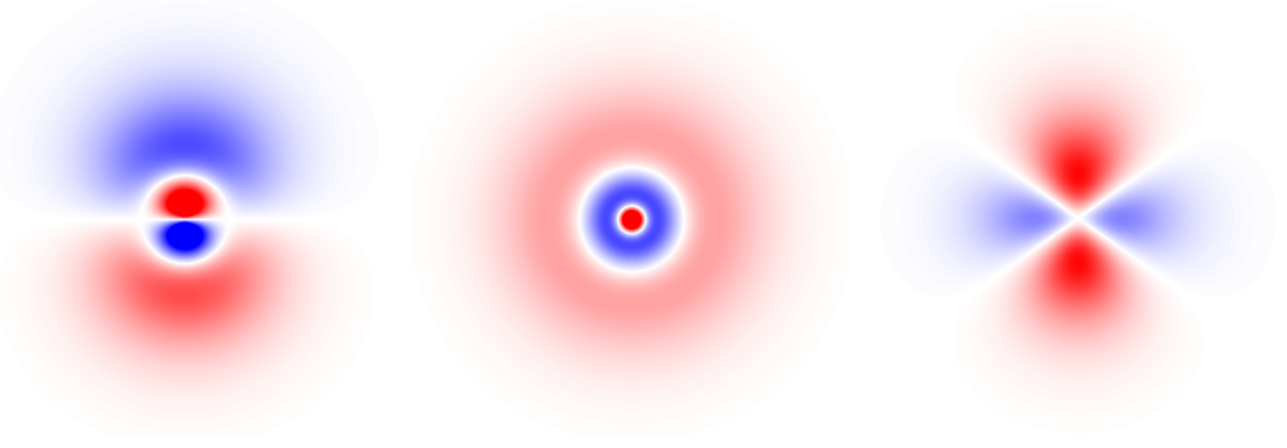


# The Non-Relativistic Hydrogen Atom



## 1 Introduction

### 1.1 The History Of The Atom

In 1911 Ernest Rutherford published the results of the now famous Geiger-Marsden experiment, which involved measuring the deflections of  $\alpha$  particles by a thin sheet of gold foil. Analysis of these deflections seemed to suggest that all of the positive charge in the gold atoms was concentrated into a dense nucleus, with the electrons orbited around it. While this was certainly a step in the right direction when compared to JJ Thomson's plum pudding model, it still left a lot to be desired.

Firstly, it had already been predicted theoretically, and confirmed experimentally, that accelerating charges loose energy in the form of electromagnetic radiation. Thus, it should not be possible for an electron to sustain a stable orbit around a nucleus, since it would just radiate away its energy and collapse into the nucleus. In fact, given the measurements available at the time, it could be shown that this collapse should occur in less than a tenth of a nanosecond.

Secondly, Rutherford's model was completely unable to account for the sharp lines seen in atomic emission spectra. As early as 1890, Johannes Rydberg had discovered that the spectrum of the hydrogen atom could be described by the formula

$$\frac{1}{\lambda} = R_H \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad n_1, n_2 \in \mathbb{Z}^+$$

where the Rydberg constant  $R_H$  was empirically measured to take a value of about  $1.10 \times 10^{-7} \text{ m}^{-1}$ . Clearly any successful model of the atom would have to reproduce this result, and if possible give an expression for  $R_H$  in terms of other more fundamental constants.

Finally, Rutherford's model was completely incapable of explaining interactions between atoms and the formations of chemical bonds, although Rutherford was still awarded the Nobel prize in chemistry for his work, which was apparently a source of great annoyance for him. This third point would only be rectified following the full development of quantum theory by the likes of Schrödinger, and Heisenberg; however, significant progress was made in the intervening time using some of the rudimentary tools of quantum mechanics.

## 1.2 The Heisenberg Uncertainty Principle

The Heisenberg uncertainty principle states that the quantum mechanical uncertainties associated with a particle's position and momentum are constrained such that

$$\sigma_x \sigma_p \geq \frac{\hbar}{2}$$

More generally, and less rigorously, we can say that, if  $r$  and  $p$  are the typical length and momentum scales of a quantum system, their product will typically be on the order of Planck's constant.

$$rp \sim \hbar$$

While this is not a strictly rigorous, or well defined result, it can be useful in allowing us to estimate the magnitudes of various quantities in a quantum system. For example, let us consider the hydrogen atom. Classically, we would say that the energy of an electron orbiting a proton would be given by

$$E = \frac{p^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r}$$

where we have neglected the kinetic energy of the proton, because it will represent a correction of less than 1 part in 1000, and this is only an estimate. If we assume that  $rp = \hbar$ , we obtain

$$E = \frac{\hbar^2}{2m_e r^2} - \frac{e^2}{4\pi\epsilon_0 r}$$

This does allow us to see why a quantum mechanical electron cannot collapse into the nucleus. Simply put, confining the electron reduces the uncertainty in its position so much that the corresponding increase in its momentum uncertainty gives it too much kinetic energy. In order to estimate the ground state of the electron, we simply find the value of  $r$  that minimises its energy. This gives us

$$E = -\frac{E_H}{2} = -\frac{1}{2} \frac{m_e e^4}{\hbar^2 16\pi^2 \epsilon_0^2} \qquad r = a_0 = \frac{\hbar^2 4\pi\epsilon_0}{m_e e^2}$$

where the constants  $a_0$  and  $E_H$  are referred to as the Bohr radius and Hartree energy respectively. As it turns out, these estimates are far better than they have any right to be (which is partially because I knew the answers I wanted when I chose to set  $rp = \hbar$  instead of any other multiple of  $\hbar$ ), because not only is the expression for the ground state energy correct, the Bohr radius is also the most probable distance of the electron from the nucleus in the ground state.

Technically speaking these results are only correct for a hydrogen atom in which the proton remains stationary, since we did not account for the kinetic energy of the proton in our original expression. Of course we had no way of knowing a priori that our results would be accurate enough for this to be relevant; however, it is fairly simple to correct this result for a real hydrogen atom. Just as in classical mechanics, we can the solution to the two body problem is obtained by taking the solution to the one body problem and simply replacing the mass  $m_e$  with the reduced mass  $\mu$ , which is defined by

$$\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_p}$$

The only other corrections that remain are those due to relativistic effects, which we shall not discuss here.

While this method is quite helpful for examining the ground state, there is no obvious generalisation that would enable us to find the excited states of the hydrogen atom. Luckily however, there is a relatively simple way of obtaining all of the energy levels, and this will be the topic of the next section.

### 1.3 The Bohr Model

In 1913 Niels Bohr proposed that, in the hydrogen atom, the electron could only occupy a circular orbit around the nucleus, and moreover, he suggested that the angular momentum of this orbit must be an integer multiple of the reduced Planck's constant  $\hbar$ . With the help of Sommerfeld, Bohr was later able to relax the restriction of circular orbits into a second quantisation condition; however, since this just makes the model more complicated, while only marginally more correct, we shall not discuss it here.

For an electron in a circular orbit of radius  $r$ , the angular velocity can be calculated by equating the centripetal force to the Coulomb attraction between the electron and proton. This gives us the expression

$$\omega^2 = \frac{e^2}{4\pi\epsilon_0\mu r^3}$$

where as before  $\mu$  is the reduced mass of the atom. Calculating the total angular momentum of this orbit, and then equating it to  $n\hbar$  gives us the following condition

$$L = \mu r^2 \omega = n\hbar \implies \frac{\mu r e^2}{\hbar^2 4\pi\epsilon_0} = n^2 \implies r = \frac{n^2 \hbar^2 4\pi\epsilon_0}{\mu e^2}$$

The total energy of the orbit is given by the expression

$$E = \frac{\mu r^2 \omega^2}{2} - \frac{e^2}{4\pi\epsilon_0 r}$$

which when expressed in terms of the quantum number  $n$ , gives us the correct expression for the energy levels in a hydrogen atom.

$$E_n = -\frac{1}{2n^2} \frac{\mu e^4}{\hbar^2 16\pi^2 \epsilon_0^2} \quad n \in \mathbb{Z}^+$$

Following on from the work of Planck and Einstein with regards to the quantisation of energy in the electromagnetic fields, we can identify that an excited hydrogen atom can only emit photons whose energies are equal to a difference between two energy levels. Thus, the wavelengths of these photons must satisfy

$$\frac{1}{\lambda} = \frac{E_{n_2} - E_{n_1}}{2\pi\hbar c} = \frac{\mu e^4}{64\hbar^3 \pi^3 \epsilon_0^2 c} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

perfectly reproducing Rydberg's formula. Quantising the energy levels in this way explains why atoms do not collapse, since the accelerating charges can not continuously radiate energy, and instead must emit it in discrete quanta. This, together with providing a theoretical justification for Rydberg's formula, made Bohr's model very appealing, and it was widely accepted. However, the model is not perfect. It still fails to predict the behaviour of even the simplest molecules, which is largely due to its inability to accurately predict the three dimensional nature of atoms.

In the following sections we shall discuss two different methods for obtaining the energy spectrum of the hydrogen atom. Firstly, we shall use standard methods of solving partial differential equations in order to obtain the wave functions of the atoms from the time independent Schödinger equation. Then we shall use operator methods to manipulate Schödinger's equation in a slightly more abstract and sophisticated manner.

## 2 The Differential Equation Approach

### 2.1 The Time Independent Schrödinger Equation

In general, the energy levels of a quantum system can be found by solving Schrödinger's eigenvalue equation

$$\hat{H}\psi = E\psi$$

where  $\hat{H}$  is a differential operator, referred to as the Hamiltonian. For simple systems, the Hamiltonian contains a Laplacian term  $\nabla^2$ , which represents the kinetic energy of the system, and some additional term for the potential energy.

A hydrogen-like atom is any atom which consists of a single electron orbiting a positively charged nucleus. If the electron has a mass  $m_e$  and charge  $-e$ , while the nucleus has a mass  $m_N$  and charge  $Ze$ , then Schrödinger's equation takes the form

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi - \frac{Ze^2\psi}{4\pi\epsilon_0 r} = E\psi$$

where  $\mu$  is the atom's reduced mass, given by

$$\mu = \frac{m_e m_N}{m_e + m_N} \implies \mu \approx m_e \text{ if } m_e \ll m_N$$

and the wave function  $\psi$  is a function of the electron's position, relative to the nucleus. Since the problem is spherically symmetric, it seems reasonable for us to express Schrödinger's equation in spherical polar coordinates  $(r, \vartheta, \varphi)$ . This gives us a partial differential equation of the form

$$-\frac{\hbar^2}{2\mu} \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin^2 \vartheta} \frac{\partial}{\partial \vartheta} \left( \sin \vartheta \frac{\partial \psi}{\partial \vartheta} \right) + \frac{1}{r^2 \sin^2 \vartheta} \frac{\partial^2 \psi}{\partial \varphi^2} \right] - \frac{Ze^2\psi}{4\pi\epsilon_0 r} = E\psi$$

We have essentially two degrees of freedom in how we can rewrite this equation, we could multiply the whole thing by a constant, or we could define a new variable  $\rho$ , which is proportional to  $r$ , and express the equation in terms of  $\rho$  instead. This is perfect, because we have two parameters in our equation ( $\mu$  and  $Z$ ), so we can remove them by recasting the equation in a more standard form. The standard way of doing this is to write that

$$-\frac{1}{2} \left[ \frac{1}{\rho^2} \frac{\partial}{\partial \rho} \left( \rho^2 \frac{\partial \phi}{\partial \rho} \right) + \frac{1}{\rho^2 \sin^2 \vartheta} \frac{\partial}{\partial \vartheta} \left( \sin \vartheta \frac{\partial \phi}{\partial \vartheta} \right) + \frac{1}{\rho^2 \sin^2 \vartheta} \frac{\partial^2 \phi}{\partial \varphi^2} \right] - \frac{\phi}{\rho} = \mathcal{E}\phi$$

where the change from  $\psi(r, \vartheta, \varphi)$  to  $\phi(\rho, \vartheta, \varphi)$  has been made to keep any mathematicians happy. The dimensionless quantities  $\rho$  and  $\mathcal{E}$  are related to  $r$  and  $E$  by the relations

$$\rho = \frac{\mu Z}{m_e} \frac{r}{a_0} = \frac{\mu Z}{m_e} \frac{m_e e^2}{\hbar^2 4\pi\epsilon_0} r \quad \mathcal{E} = \frac{m_e}{Z^2 \mu} \frac{E}{E_H} = \frac{m_e}{Z^2 \mu} \frac{\hbar^2 16\pi^2 \epsilon_0^2}{m_e e^4} E$$

where the constants  $a_0$  and  $E_H$  are the Bohr radius and the Hartree energy, just as we had before. This procedure of nondimensionalisation is essentially equivalent to adopting the natural system of units for the problem at hand. Our task is now to find the appropriate functions  $\phi$  for which this equation holds. Importantly, these solutions must be physical, which means that they must obey certain smoothness conditions, and they must be suitably normalisable. These restrictions will then restrict  $\mathcal{E}$  to only take on certain discrete values.

## 2.2 Separation Of Variables

One of the most powerful ways of solving linear partial differential equations is Fourier's method of separating the variables. In order to apply this method, we first assume that our solution can be represented in the separable form

$$\phi(\rho, \vartheta, \varphi) = R(\rho)T(\vartheta)I(\varphi)$$

Substituting this expression into Schrödinger's equation, and dividing the whole thing through by  $\phi$  yields

$$\frac{\rho^2 R''(\rho) + 2\rho R'(\rho) + 2\rho R(\rho)}{\rho^2 R(\rho)} + \frac{\sin \vartheta T''(\vartheta) + \cos \vartheta T'(\vartheta)}{\rho^2 \sin \vartheta T(\vartheta)} + \frac{I''(\varphi)}{\rho^2 \sin^2 \vartheta I(\varphi)} = -2\mathcal{E}$$

Since the right hand side of this equation is simply a constant, the left hand side must also be a constant. However, the only way this can be true is for the  $\varphi$  dependence in the final term to cancel out. In other words, there must exist some constant  $\xi$  such that

$$\frac{I''(\varphi)}{I(\varphi)} = \xi \implies \frac{d^2 I}{d\varphi^2} - \xi I(\varphi) = 0$$

Similarly, the  $\vartheta$  dependence from the second two terms must also cancel out. By inserting the constant  $\xi$  to remove the  $\varphi$  dependence, this allows us to generate an ordinary differential equation for  $T$

$$\frac{\sin \vartheta T''(\vartheta) + \cos \vartheta T'(\vartheta)}{\sin \vartheta T(\vartheta)} + \frac{\xi}{\sin^2 \vartheta} = \eta \implies \frac{1}{\sin \vartheta} \frac{d}{d\vartheta} \left( \sin \vartheta \frac{dT}{d\vartheta} \right) + \frac{\xi T(\vartheta)}{\sin^2 \vartheta} - \eta T(\vartheta) = 0$$

where  $\eta$  is simply another separation constant. This then reduces the Schrödinger equation into an ordinary differential equation for  $R(\rho)$

$$\rho^2 \frac{d^2 R}{d\rho^2} + 2\rho \frac{dR}{d\rho} + (2\mathcal{E}\rho^2 + 2\rho + \eta)R(\rho) = 0$$

We shall now address each of these ordinary differential equations in turn, and as we shall discover, each of them has analytic solutions, provided certain restrictions are imposed on  $\xi$ ,  $\eta$ , and  $\mathcal{E}$ .

## 2.3 The Azimuthal Equation

The ordinary differential equation

$$\frac{d^2 I}{d\varphi^2} - \xi I(\varphi) = 0$$

is by far the simplest of those that we have to consider, and as such, has the simplest solutions. To solve this equation, simply note that the integrating factors  $e^{\pm\sqrt{\xi}\varphi}$  allow it to be written as

$$e^{\sqrt{\xi}\varphi} \frac{d}{d\varphi} \left[ e^{-2\sqrt{\xi}\varphi} \frac{d}{d\varphi} \left( I(\varphi) e^{\sqrt{\xi}\varphi} \right) \right] = 0$$

Integrating this equation then immediately leads us to the general solution

$$I(\varphi) = Ae^{\sqrt{\xi}\varphi} + Be^{-\sqrt{\xi}\varphi}$$

Since the wave function must be continuous and single valued, we require that  $I(\varphi + 2\pi) = I(\varphi)$ , which can only be possible if  $\sqrt{\xi} = im$  for some integer  $m$ , referred to as the magnetic quantum number. Thus, we identify

$$I_m(\varphi) = \frac{e^{im\varphi}}{\sqrt{2\pi}} \quad \xi = -m^2$$

where  $m$  can be either positive or negative. The normalisation constant is chosen such that

$$\int_0^{2\pi} I_{m'}(\varphi)^* I_m(\varphi) d\varphi = \delta_{mm'}$$

## 2.4 The Polar Equation

Compared to the azimuthal equation, the polar equation is significantly more complicated. However, we can still find an analytic solution. Starting with the equation

$$\frac{1}{\sin \vartheta} \frac{d}{d\vartheta} \left( \sin \vartheta \frac{dT}{d\vartheta} \right) - \frac{m^2 T(\vartheta)}{\sin^2 \vartheta} - \eta T(\vartheta) = 0$$

It is conventional for us to make the substitution  $T(\vartheta) = F(\cos \vartheta)$ , and to then rewrite the equation in terms of the variable  $u = \cos \vartheta$ . This leads us to obtain the generalised Legendre equation

$$(u^2 - 1) \frac{d^2 F}{du^2} + 2u \frac{dF}{du} - \frac{m^2 F(u)}{u^2 - 1} + \eta F(u) = 0$$

As we shall see, insisting that  $F$  be finite at  $u = \pm 1$ , which is necessary for the wave function to be finite at the poles, requires that  $\eta = -\ell(\ell + 1)$ , where  $\ell \geq |m|$  is an integer. The solutions to this equation are well known to be the associated Legendre functions, which gives us the result that

$$T_\ell^m(\vartheta) = \sqrt{\frac{(2\ell + 1)(\ell - m)!}{2(\ell + m)!}} P_\ell^m(\cos \vartheta)$$

where the normalisation has been chosen such that, for fixed  $m$

$$\int_0^\pi T_{\ell'}^m(\vartheta) T_\ell^m(\vartheta) \sin \vartheta d\vartheta = \delta_{\ell\ell'}$$

We can then combine the two angular parts of our wave function in order to obtain the spherical harmonics, which are defined such that

$$Y_\ell^m(\vartheta, \varphi) = T_\ell^m(\vartheta) I_m(\varphi) = \sqrt{\frac{(2\ell + 1)(\ell - m)!}{4\pi(\ell + m)!}} P_\ell^m(\cos \vartheta) e^{im\varphi}$$

The orthogonality relation for the spherical harmonics then follows directly from the orthogonality relations of their constituent functions

$$\int_{\vartheta=0}^\pi \int_{\varphi=0}^{2\pi} Y_{\ell'}^{m'}(\vartheta, \varphi)^* Y_\ell^m(\vartheta, \varphi) \sin \vartheta d\varphi d\vartheta = \delta_{\ell'\ell} \delta_{mm'}$$

Another, less obvious, property of the spherical harmonics is that they form a complete basis for functions on the surface of a sphere. This follows directly from the completeness of the trigonometric functions on the intervals  $[0, 2\pi]$  and  $[0, \pi]$  respectively. The first few spherical harmonics are listed below.

$\ell$	$m$	$Y_\ell^m(\vartheta, \varphi)$	2	-2	$\sqrt{\frac{15}{32\pi}} \sin^2 \vartheta e^{-2i\varphi}$
0	0	$\sqrt{\frac{1}{4\pi}}$	2	-1	$\sqrt{\frac{15}{32\pi}} \sin 2\vartheta e^{-i\varphi}$
1	-1	$\sqrt{\frac{3}{8\pi}} \sin \vartheta e^{-i\varphi}$	2	0	$\sqrt{\frac{15}{16\pi}} (3 \cos^2 \vartheta - 1)$
1	0	$\sqrt{\frac{3}{8\pi}} \cos \vartheta$	2	1	$-\sqrt{\frac{15}{32\pi}} \sin 2\vartheta e^{i\varphi}$
1	-1	$-\sqrt{\frac{3}{8\pi}} \sin \vartheta e^{i\varphi}$	2	2	$\sqrt{\frac{15}{32\pi}} \sin^2 \vartheta e^{2i\varphi}$

## 2.5 Legendre Polynomials

Before we consider the solutions to the generalised Legendre equation, it is helpful for us to discuss the special case of  $m = 0$ , in which case we simply obtain Legendre's equation.

$$(u^2 - 1)\frac{d^2 F}{du^2} + 2u\frac{dF}{du} - \ell(\ell + 1)F(u) = 0$$

The first thing for us to do is to establish what values of  $\ell$  are permitted. Rearranging Legendre's equation somewhat, we can see that

$$\frac{d^2 F}{du^2} = \frac{\ell(\ell + 1)F(u) - 2u\frac{dF}{du}}{u^2 - 1}$$

which implies that as long as  $F$  and its first derivative are continuous at a point (except  $u = \pm 1$ ), the second derivative will also be continuous at that point. We can then differentiate this result to show that all further derivatives of  $F$  must be continuous at that point. Thus, the only points at which any lack of smoothness can enter into  $F$  are unsurprisingly at  $u = \pm 1$ . If we require that  $F(\pm 1)$  remains finite, then the problematic denominator term must cancel out near the singularity, in order to prevent the derivatives and hence the function itself from growing unboundedly, which means that  $F$  must be perfectly smooth everywhere.

Let us now consider what happens to  $F$  as  $u \rightarrow \infty$ . In this limit Legendre's equation becomes the Euler-Cauchy equation

$$u^2 \frac{d^2 F}{du^2} + 2u \frac{dF}{du} - \ell(\ell + 1)F(u) \approx 0$$

There are several ways of solving an Euler-Cauchy equation. One of the most elegant methods is to make the substitution  $u = e^w$ , in which case it reduces to a linear ODE with constant coefficients. Another similar method is to make use of an integrating factor of the form  $u^n$  to reduce it to a first order equation. However, the easiest method is simply to recognise that the solutions take the form of monomials  $u^n$ , and to just solve for  $n$ . This tells us that\*

$$F(u) \approx Au^\ell + bu^{-\ell-1} \approx Au^\ell$$

If we substitute  $u^\ell$  back into Legendre's equation, we can see that we will only need a term of order  $u^{\ell-2}$  to correct for its deviation from the solution. This term will then need an order  $u^{\ell-4}$  correction, and so on. The only way for this to be smooth at the origin is if all of these powers are non-negative integers, which means that  $\ell \in \mathbb{Z}^{\geq 0}$ .

Now we come to the task of actually solving Legendre's equation. There are many ways of doing this; however, one of the most elegant is to rewrite the equation in terms of a new function  $G(u)$ , such that

$$F(u) = \frac{d^\ell G}{du^\ell}$$

Adding and subtracting some extra terms then allows us to write the original equation in the form

$$(u^2 - 1)\frac{d^{\ell+2} G}{du^{\ell+2}} + 2(\ell + 1)u\frac{d^{\ell+1} G}{du^{\ell+1}} + \ell(\ell + 1)\frac{d^\ell G}{du^\ell} - 2\ell u\frac{d^{\ell+1} G}{du^{\ell+1}} - 2\ell(\ell + 1)\frac{d^\ell G}{du^\ell} = 0$$

Using Leibniz's formula we can then collect all the terms together into a single  $(\ell + 1)$ th derivative to give

$$\frac{d^{\ell+1}}{du^{\ell+1}} \left[ (u^2 - 1)\frac{dG}{du} - 2\ell uG(u) \right] = 0$$

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\*we can assume  $\ell > -(\ell + 1)$  without loss of generality, because  $\ell(\ell + 1)$  is symmetric about  $-\frac{1}{2}$ .

We can then integrate this equation  $\ell + 1$  times in order to obtain a first order ODE for  $G$ . Now technically speaking, this should lead to constants of integration and powers of  $u$  on the left hand side of the equation; however, if we want  $G$  to be finite at  $\pm 1$ , it turns out that we need to set all of the integration constants to zero. Thus, we obtain

$$(u^2 - 1) \frac{dG}{du} - 2\ell u G(u) = 0$$

To solve this equation, we simply multiply through by the integrating factor  $(u^2 - 1)^{-\ell-1}$ , which gives us

$$\frac{1}{(u^2 - 1)^\ell} \frac{dG}{du} - \frac{2\ell u}{(u^2 - 1)^{\ell+1}} G(u) = \frac{d}{du} \left( \frac{G(u)}{(u^2 - 1)^\ell} \right) = 0 \implies G(u) = A(u^2 - 1)^\ell$$

If we now define the  $\ell$ th Legendre polynomial  $P_\ell$  to be the solution of Legendre's equation such that  $P_\ell(1) = 1$ , we can use this result to obtain Rodrigues' formula

$$P_\ell(u) = \frac{1}{2^\ell \ell!} \frac{d^\ell}{du^\ell} (u^2 - 1)^\ell$$

We can use Rodrigues' formula to establish several useful properties of the Legendre polynomials. For example, if we evaluate one of the derivatives in the expression for  $P_{\ell+1}$ , and then expand the rest using Leibniz's formula, we obtain

$$P_{\ell+1}(u) = \frac{1}{2^\ell \ell!} \frac{d^\ell}{du^\ell} u(u^2 - 1)^\ell = u P_\ell(u) + \ell \int_{-1}^u P_\ell(u') du'$$

Differentiating this result then removes the integral and leaves us with

$$\frac{dP_{\ell+1}}{du} = (\ell + 1) P_\ell(u) + u \frac{dP_\ell}{du}$$

Alternatively, we could first manually evaluate the second derivative

$$\frac{d^2}{du^2} (u^2 - 1)^{\ell+1} = 2(\ell + 1)(2\ell + 1)(u^2 - 1)^\ell + 4\ell(\ell + 1)(u^2 - 1)^{\ell-1}$$

then differentiate this  $\ell$  times in order to obtain the relationship that

$$(2\ell + 1) P_\ell(u) = \frac{dP_{\ell+1}}{du} - \frac{dP_{\ell-1}}{du}$$

Since  $P_\ell(-u) = (-1)^\ell P_\ell(u)$ , and  $P_\ell(1) = 1$ , we can definitely say that  $P_{\ell+1}(-1) = P_{\ell-1}(-1)$ . Thus, we can use this relationship to quickly evaluate the integral in our expression for  $P_{\ell+1}$ , which yields Bonnet's recurrence relation

$$(\ell + 1) P_{\ell+1}(u) = (2\ell + 1) u P_\ell(u) - \ell P_{\ell-1}(u)$$

One relationship that would be particularly useful would be if we could express  $P_{\ell+1}(u)$  purely in terms of  $P_\ell(u)$ . In order to find this relationship, we can first write down Legendre's equation

$$P_{\ell+1}(u) = \frac{u^2 - 1}{(\ell + 1)(\ell + 2)} \frac{d^2 P_{\ell+1}}{du^2} + \frac{2u}{(\ell + 1)(\ell + 2)} \frac{dP_{\ell+1}}{du}$$

We can then substitute in our expression for the derivative of  $P_{\ell+1}$  in terms of  $P_\ell$ , and after some rearrangement we are left with

$$P_{\ell+1}(u) = \frac{u}{(\ell + 1)(\ell + 2)} \left[ (u^2 - 1) \frac{d^2 P_\ell}{du^2} + 2u \frac{dP_\ell}{du} - \ell(\ell + 1) P_\ell \right] + \frac{u^2 - 1}{\ell + 1} \frac{dP_\ell}{du} + u P_\ell(u)$$



which, after substituting in Legendre's equation for  $P_\ell$ , gives rise to the relatively simple recurrence relation

$$P_{\ell+1}(u) = uP_\ell(u) + \frac{u^2 - 1}{\ell + 1} \frac{dP_\ell}{du}$$

Rodrigues' formula is most useful when it comes to determining the orthogonality condition of the Legendre polynomials. Let us consider the integral

$$\int_{-1}^1 P_{\ell'}(u)P_\ell(u) du = \frac{1}{2^{\ell'+\ell}\ell'!\ell!} \int_{-1}^1 \frac{d^{\ell'}}{du^{\ell'}}(u^2 - 1)^{\ell'} \frac{d^\ell}{du^\ell}(u^2 - 1)^\ell du$$

where we shall assume without loss of generality that  $\ell' \geq \ell$ . Integrating by parts  $\ell'$  times, and noting that all of the boundary terms vanish, we find that

$$\int_{-1}^1 P_{\ell'}(u)P_\ell(u) du = \frac{(-1)^{\ell'}}{2^{\ell'+\ell}\ell'!\ell!} \int_{-1}^1 (u^2 - 1)^{\ell'} \frac{d^{\ell+\ell'}}{du^{\ell+\ell'}}(u^2 - 1)^\ell du$$

Clearly, if  $\ell' > \ell$ , then the integrand will be equal to zero, and hence we can conclude that the  $P_\ell$  are mutually orthogonal functions. In the case that  $\ell' = \ell$ , we can then simplify our expression to obtain

$$\int_{-1}^1 P_\ell(u)^2 du = \frac{(-1)^\ell(2\ell)!}{2^{2\ell}(\ell!)^2} \int_{-1}^1 (u^2 - 1)^\ell du$$

We can evaluate this integral fairly easily by using a reduction formula. That is to say that, if we let

$$K_\ell = \int_{-1}^1 (u^2 - 1)^\ell du$$

then we can integrate by parts in order to obtain

$$K_\ell = -2\ell \int_{-1}^1 u^2(u^2 - 1)^{\ell-1} du = -2\ell(K_{\ell-1} + K_\ell)$$

We can thus express  $K_\ell$  in terms of  $K_{\ell-1}$ . This then enables us to conclude that

$$K_\ell = -\frac{2\ell}{2\ell + 1} K_{\ell-1} \implies K_\ell = \frac{(-1)^\ell 2^\ell \ell! 2^\ell \ell!}{(2\ell + 1)!} K_0$$

Since  $K_0$  is trivially equal to 2, we find that

$$\int_{-1}^1 P_{\ell'}(u)P_\ell(u) du = \frac{2}{2\ell + 1} \delta_{\ell\ell'}$$

Thus, if we wish to construct a set of orthonormal functions from the solutions to Legendre's equation, we should simply use the appropriately scaled Legendre polynomials

$$F_\ell(u) = \sqrt{\frac{2\ell + 1}{2}} P_\ell(u)$$

The first few Legendre polynomials are presented below.

$\ell$	$P_\ell(u)$	$\ell$	$P_\ell(u)$	$\ell$	$P_\ell(u)$
0	1	2	$\frac{3u^2}{2} - \frac{1}{2}$	4	$\frac{35x^4}{8} - \frac{30x^2}{8} + \frac{3}{8}$
1	$u$	3	$\frac{5u^3}{2} - \frac{3u}{2}$	5	$\frac{63x^5}{8} - \frac{70x^3}{8} + \frac{15x}{8}$

## 2.6 Associated Legendre Functions

The generalised Legendre equation is closely related to Legendre's equation, taking the form

$$(u^2 - 1) \frac{d^2 F}{du^2} + 2u \frac{dF}{du} - \frac{m^2 F(u)}{u^2 - 1} - \ell(\ell + 1)F(u) = 0$$

The first thing we can note is that, for non-zero  $m$ , the requirement that  $F$  be finite at  $\pm 1$  immediately imposes the stronger restriction that  $F(\pm 1) = 0$ . To see this, let us make the substitution  $u = 1 - \delta$ , and rewrite the equation for  $\delta \ll 1$ . This gives us

$$4\delta^2 \frac{d^2 F}{d\delta^2} + 4\delta \frac{dF}{d\delta} - m^2 F(1 - \delta) \approx 0$$

This is an Euler-Cauchy equation, and together with the requirement that  $F$  be finite, it implies that  $F \approx A\delta^{\frac{|m|}{2}}$  in the neighbourhood of the point. An identical argument can be used to describe the behaviour around  $u = -1$  as well. It is worth highlighting that we are not particularly worried about what happens for negative  $\delta$ , since we only need solutions on the interval  $[-1, 1]$ . Based on this result, it seems like it might be a good idea to define

$$F(u) = (-1)^m (1 - u^2)^{\frac{m}{2}} G(u)$$

The factor of  $(-1)^m$  is known as the Condon-Shortley phase and is simply added by convention. Now technically what we are about to do is valid only for positive  $m$ ; however, the final result ends up being equally valid for negative  $m$  as well. Furthermore, since only  $m^2$  actually features in the equation, the solutions for  $-m$  must simply be scaled versions of the solutions for  $m$ . Substituting our ansatz into the generalised Legendre equation, we find that

$$(u^2 - 1) \frac{d^2 G}{du^2} + 2(1 + m)u \frac{dG}{du} + m(m + 1)G(u) - \ell(\ell + 1)G(u) = 0$$

The trick to solving this equation is to note that, if we take Legendre's equation

$$(u^2 - 1) \frac{d^2 P_\ell}{du^2} + 2u \frac{dP_\ell}{du} - \ell(\ell + 1)P_\ell(u) = 0$$

and differentiate it  $m$  times, we obtain

$$(u^2 - 1) \frac{d^2}{du^2} \frac{d^m P_\ell}{du^m} + 2(1 + m) \frac{d}{du} \frac{d^m P_\ell}{du^m} + m(m + 1) \frac{d^m P_\ell}{du^m} - \ell(\ell + 1) \frac{d^m P_\ell}{du^m} = 0$$

Thus, we can identify the associated Legendre function of order  $m$  and degree  $\ell$  as being given by the expression

$$P_\ell^m(u) = (-1)^m (1 - u^2)^{\frac{m}{2}} \frac{d^m P_\ell}{du^m} = \frac{(-1)^m}{2^\ell \ell!} (1 - u^2)^{\frac{m}{2}} \frac{d^{\ell+m}}{du^{\ell+m}} (u^2 - 1)^\ell$$

Thus, the generalised Legendre equation inherits the restriction that  $\ell$  must be an integer directly from the Legendre equation. However, in order for the solutions to be non zero, we must also have the additional constraint that  $\ell \geq |m|$ . Since both positive and negative values of  $m$  generate the same generalised Legendre equation, there must exist some constant  $c_\ell^m$  such that

$$P_\ell^{-m}(u) = c_\ell^m P_\ell^m(u) \implies \frac{d^{\ell-m}}{du^{\ell-m}} (u^2 - 1)^\ell = c_\ell^m (1 - u^2)^m \frac{d^{\ell+m}}{du^{\ell+m}} (u^2 - 1)^\ell$$

Equating the terms of order  $u^{\ell+m}$  on each side of this equation, we can conclude that

$$P_\ell^{-m}(u) = (-1)^m \frac{(\ell - m)!}{(\ell + m)!} P_\ell^m(u)$$

The associated Legendre functions possess a large number of special properties, just as the normal Legendre polynomials do; however, the most useful for us are the recursion relations in  $m$  and  $\ell$ . It follows directly from the definition of  $P_\ell^m$  that

$$\frac{dP_\ell^m}{du} = -\frac{muP_\ell^m(u)}{1-u^2} - \frac{P_\ell^{m+1}(u)}{\sqrt{1-u^2}}$$

which can then be rearranged to express  $P_\ell^{m+1}$  in terms of  $P_\ell^m$ .

$$P_\ell^{m+1}(u) = -\left[\sqrt{1-u^2} \frac{dP_\ell^m}{du} + \frac{muP_\ell^m(u)}{\sqrt{1-u^2}}\right]$$

We can use our earlier result to flip the signs of the orders in this expression, which gives us an expression for  $P_\ell^{-m-1}$  in terms of  $P_\ell^{-m}$ . Relabelling slightly then gives us

$$P_\ell^{m-1}(u) = \frac{1}{\ell(\ell+1) - m(m-1)} \left[ \sqrt{1-u^2} \frac{dP_\ell^m}{du} - \frac{muP_\ell^m(u)}{\sqrt{1-u^2}} \right]$$

If instead we wish to raise the value of  $\ell$ , we should first start with the relationship for Legendre polynomials that

$$P_{\ell+1}(u) = uP_\ell(u) + \frac{u^2-1}{\ell+1} \frac{dP_\ell}{du}$$

We can then differentiate this  $m$  times, and multiply by  $(-1)^m(1-u^2)^{\frac{m}{2}}$ , which gives us the result that

$$P_{\ell+1}^m(u) = \frac{(\ell+1-2m)u}{\ell+1} P_\ell^m(u) + \frac{\sqrt{1-u^2}}{\ell+1} P_\ell^{m+1} - \frac{m(m+\ell)\sqrt{1-u^2}}{\ell+1} P_\ell^{m-1}$$

Finally, we can substitute in our recursion relations in  $m$  in order to find an expression for  $P_{\ell+1}^m$  in terms of  $P_\ell^m$ .

$$P_{\ell+1}^m(u) = \frac{\ell+1}{\ell+1-m} \left( uP_\ell^m(u) + \frac{u^2-1}{\ell+1} \frac{dP_\ell^m}{du} \right)$$

We can also obtain an orthogonality relation for generalised Legendre functions of the same order. A neat trick for integrating the product of generalised Legendre functions is to flip the order of one, such that the  $(1-u^2)^{\frac{m}{2}}$  terms cancel. This gives us

$$J_{\ell'\ell}^m = \int_{-1}^1 P_{\ell'}^m(u) P_\ell^m(u) du = (-1)^m \frac{(\ell+m)!}{(\ell-m)!} \int_{-1}^1 P_{\ell'}^{-m}(u) P_\ell^m(u) du$$

Substituting in the definitions of the generalised Legendre functions yields

$$J_{\ell'\ell}^m = \frac{(\ell+m)!}{(\ell-m)!} \frac{(-1)^m}{2^{\ell'+\ell}\ell'!\ell!} \int_{-1}^1 \frac{d^{\ell'-m}}{du^{\ell'-m}} (u^2-1)^{\ell'} \frac{d^{\ell+m}}{du^{\ell+m}} (u^2-1)^\ell du$$

Integrating by parts  $m$  times allows us to rewrite this integral as

$$J_{\ell'\ell}^m = \frac{(\ell+m)!}{(\ell-m)!} \frac{1}{2^{\ell'+\ell}\ell'!\ell!} \int_{-1}^1 \frac{d^{\ell'-m}}{du^{\ell'}} (u^2-1)^{\ell'} \frac{d^\ell}{du^\ell} (u^2-1)^\ell du = \frac{(\ell+m)!}{(\ell-m)!} \int_{-1}^1 P_{\ell'}(u) P_\ell(u) du$$

Luckily, we already know the answer to this integral, since it is nothing more than the orthogonality relation for two Legendre polynomials. As such, we can say that

$$J_{\ell'\ell}^m = \int_{-1}^1 P_{\ell'}^m(u) P_\ell^m(u) du = \frac{2(\ell+m)!}{(2\ell+1)(\ell-m)!} \delta_{\ell\ell'}$$

## 2.7 The Radial Equation

Finally, we come to solving for the radial part of the wave function. Unfortunately for us, the radial equation takes after the polar equation in terms of the effort required to solve it. The equation in question takes the form

$$\rho^2 \frac{d^2 R}{d\rho^2} + 2\rho \frac{dR}{d\rho} + (2\mathcal{E}\rho^2 + 2\rho - \ell(\ell+1))R(\rho) = 0$$

The first thing we can do is look for the asymptotic behaviour of the solution. In the limit as  $\rho \rightarrow 0$ , we obtain yet another Euler-Cauchy equation

$$\rho^2 \frac{d^2 R}{d\rho^2} + 2\rho \frac{dR}{d\rho} - \ell(\ell+1)R(\rho) \approx 0$$

The two solutions to this equation are  $\rho^\ell$  and  $\rho^{-\ell-1}$ ; however, we can reject the second solution because it would make the wave function singular at the origin, which would cause the particle's energy to diverge. Furthermore, for  $\ell > 0$  the singularity would make the wave function non-normalisable, whereas for  $\ell = 0$ , the Laplacian of  $\rho^{-1}$  vanishes, so it clearly can't be a solution.

As  $\rho \rightarrow \infty$ , we find that the equation can be simplified to give

$$\frac{d^2 R}{d\rho^2} + 2\mathcal{E}R(\rho) \approx 0$$

Introducing the new parameter  $n$  such that  $\mathcal{E} = -\frac{1}{2n^2}$ , we find that the asymptotic behaviour of  $R$  is to go as  $e^{-\frac{\rho}{n}}$ . This motivates us to express the radial function in the form

$$R(\rho) = W(\rho)\rho^\ell e^{-\frac{\rho}{n}}$$

Substituting this back into our original differential equation yields

$$n\rho \frac{d^2 W}{d\rho^2} + 2(n(\ell+1) - \rho) \frac{dW}{d\rho} + 2(n - (1+\ell))W(\rho) = 0$$

This equation has two degrees of freedom; we can multiply the whole thing by a constant, and we can rescale the variable  $\rho$ . The conventional choice of scaling for an equation of this type is to set the coefficients of  $\rho W''$  and  $\rho W'$  equal to one and minus one respectively. This is done by dividing the whole equation by two, and introducing the substitution

$$W(\rho) = Q(\varrho) \qquad \varrho = \frac{2\rho}{n}$$

This leads us to the generalised Laguerre equation

$$\varrho \frac{d^2 Q}{d\varrho^2} + (2\ell + 1 + 1 - \varrho) \frac{dQ}{d\varrho} + (n - (\ell + 1))Q(\varrho) = 0$$

The solutions to this equation are known to be the generalised Laguerre polynomials, which allows us to say that

$$R_{n\ell}(\rho) = \sqrt{\frac{8}{n^3} \frac{(n-\ell-1)!}{2n(n+\ell)!}} \left(\frac{2\rho}{n}\right)^\ell L_{n-\ell-1}^{2\ell+1}\left(\frac{2\rho}{n}\right) e^{-\frac{\rho}{n}}$$

These solutions only exist if  $n - (\ell + 1)$  is a non-negative integer, which implies that  $n > \ell$  must be an integer. This gives rise to the expected quantisation of the energies

$$\mathcal{E}_n = -\frac{1}{2n^2} \quad n \in \mathbb{Z}^+$$

with each energy level having a degeneracy of  $n^2$ .

## 2.8 Laguerre Polynomials

The Laguerre polynomials are defined as the solutions of Laguerre's equation

$$\varrho \frac{d^2 Q}{d\varrho^2} + (1 - \varrho) \frac{dQ}{d\varrho} + kQ(\varrho) = 0$$

Subject to the restrictions that they are equal to one at the origin, and they grow slower than an exponential as  $\varrho \rightarrow \infty$ . This condition allows us to determine the asymptotic behaviour of the Laguerre polynomials by noting that, as  $\varrho \rightarrow \infty$ , the equation becomes

$$\varrho \frac{dQ}{d\varrho} - kQ(\varrho) \approx 0$$

which directly implies that  $Q \approx A\varrho^k$ . Substituting this term back into Laguerre's equation, we can see that its deviation from the true solution is a correction of order  $\varrho^{k-1}$ . This then elicits a correction of order  $\varrho^{k-2}$  and so on. If we wish to avoid negative powers of  $\varrho$  then we must find that  $k$  is a non negative integer.

One method of solving Laguerre's equation is to write the solution in terms of a contour integral in the complex plane. That is to say, we assume that there exists a function  $U(z)$  such that

$$Q(\varrho) = \oint_{\Gamma} U(z) e^{\varrho z} dz$$

for any closed contour  $\Gamma$ , which encloses the origin. Substituting this into Laguerre's equation, and integrating by parts to remove the  $\varrho$  terms, we obtain

$$\oint_{\Gamma} \left\{ (k+1-z)U(z) - z(z-1) \frac{dU}{dz} \right\} e^{\varrho z} dz = 0$$

Requiring that this holds true for arbitrary values of  $\Gamma$  gives us a first order differential equation for  $U(z)$ . Thus, we conclude that

$$\frac{dU}{dz} = \frac{k+1-z}{z(z-1)} \implies U(z) = A \frac{(z-1)^k}{z^{k+1}}$$

In order to evaluate the resulting contour integral, we will need to make use of the residue theorem. The residue theorem is essentially a statement that, for any closed loop  $\Gamma$  around the origin

$$\oint_{\Gamma} z^n dz = \begin{cases} 2\pi i & n = -1 \\ 0 & \text{otherwise} \end{cases}$$

As such, finding the Laguerre polynomials is no more complicated than finding the coefficient of the  $z^{-1}$  term in a Laurent series expansion of the integrand. Thus, we can say that

$$L_k(\varrho) = \frac{1}{2\pi i} \oint \frac{(z-1)^k e^{\varrho z}}{z^{k+1}} dz = \frac{1}{k!} \frac{d^k}{dz^k} (z-1)^k e^{\varrho z} \Big|_{z=0} = \frac{1}{k!} \left( \frac{d}{dz} + \varrho \right)^k z^k \Big|_{z=-1}$$

Based on the symmetry of the binomial coefficients, we can say that

$$\left( \frac{d}{dz} + \varrho \right)^k z^k = \left( \frac{d}{d\varrho} + z \right)^k \varrho^k$$

which immediately gives us the Rodrigues formula for the Laguerre polynomials

$$L_k(\varrho) = \frac{1}{k!} \left( \frac{d}{d\varrho} - 1 \right)^k \varrho^k = \frac{e^{\varrho}}{k!} \frac{d^k}{d\varrho^k} \left( e^{-\varrho} \varrho^k \right)$$

The Laguerre polynomials have a number of different orthogonality relations depending on the weighting function that is used to define the inner product; however, in most cases this final expression will be the most useful for actually evaluating the necessary integrals.

## 2.9 Generalised Laguerre Polynomials

We can generalise Laguerre's equation somewhat by adding in an extra parameter  $\alpha$ . The most useful place to add this parameter turns out to be in front of the single derivative term, yielding the generalised Laguerre equation

$$\varrho \frac{d^2 Q}{d\varrho^2} + (\alpha + 1 - \varrho) \frac{dQ}{d\varrho} + kQ(\varrho) = 0$$

It turns out that we can obtain generalised Laguerre polynomials for any value of  $\alpha$ ; however, it will be convenient for us to start by assuming that  $\alpha$  is a positive integer, and then simply verifying that the resulting expression holds for arbitrary  $\alpha$ .

The first step in solving the equation is to note that, if we take the standard Laguerre equation

$$\varrho \frac{d^2 L_{k+\alpha}}{d\varrho^2} + (1 - \varrho) \frac{dL_{k+\alpha}}{d\varrho} + (k + \alpha)L_{k+\alpha}(\varrho) = 0$$

and differentiate it  $\alpha$  times, we obtain

$$\varrho \frac{d^2}{d\varrho^2} \frac{d^\alpha L_{k+\alpha}}{d\varrho^\alpha} + (\alpha + 1 - \varrho) \frac{d}{d\varrho} \frac{d^\alpha L_{k+\alpha}}{d\varrho^\alpha} + k \frac{d^\alpha L_{k+\alpha}}{d\varrho^\alpha} = 0$$

By convention, we can then identify the associated Laguerre polynomial as being

$$L_k^\alpha(\varrho) = (-1)^\alpha \frac{d^\alpha L_{k+\alpha}}{d\varrho^\alpha} = \frac{(-1)^\alpha}{(k + \alpha)!} \left( \frac{d}{d\varrho} - 1 \right)^{k+\alpha} \frac{d^\alpha \varrho^{k+\alpha}}{d\varrho^\alpha} = \frac{(-1)^\alpha}{k!} \left( \frac{d}{d\varrho} - 1 \right)^{k+\alpha} \varrho^k$$

By expanding out this expression with the standard binomial coefficients, and simply considering each power of  $\varrho$  in the resulting expression, we can see that this is equivalent to

$$L_k^\alpha(\varrho) = \frac{(-1)^\alpha}{k!} \left( \frac{d}{d\varrho} - 1 \right)^{k+\alpha} \varrho^k = \frac{\varrho^{-\alpha}}{k!} \left( \frac{d}{d\varrho} - 1 \right)^k \varrho^{k+\alpha} = \frac{e^\varrho \varrho^{-\alpha}}{k!} \frac{d^k}{d\varrho^k} \left( e^{-\varrho} \varrho^{k+\alpha} \right)$$

This final expression can accept arbitrary values of  $\alpha$ , and it is a simple matter to substitute it back into the generalised Laguerre equation to verify that this is valid.

Just as with the standard Laguerre polynomials, these solutions obey a number of orthogonality relations; however the one we are interested in features integrals of the form

$$C_k^\alpha = \int_0^\infty \varrho^{\alpha+1} e^{-\varrho} L_k^\alpha(\varrho) L_k^\alpha(\varrho) d\varrho = \frac{1}{k!k!} \int_0^\infty \varrho^{\alpha+1} e^\varrho \frac{d^{k+\alpha}}{d\varrho^{k+\alpha}} \left( e^{-\varrho} \varrho^k \right) \frac{d^{k+\alpha}}{d\varrho^{k+\alpha}} \left( e^{-\varrho} \varrho^k \right) d\varrho$$

Integrating by parts  $k + \alpha$  times yields

$$C_k^\alpha = \frac{(-1)^{k+\alpha}}{k!k!} \int_0^\infty e^{-\varrho} \varrho^k \frac{d^{k+\alpha}}{d\varrho^{k+\alpha}} \left( \varrho^{\alpha+1} e^\varrho \frac{d^{k+\alpha}}{d\varrho^{k+\alpha}} \left( e^{-\varrho} \varrho^k \right) \right) d\varrho$$

Explicitly evaluating the derivative is fairly tedious work, but it is doable, so long as we note that most of the terms end up vanishing from the overall expression. This gives us the result that

$$\frac{d^{k+\alpha}}{d\varrho^{k+\alpha}} \left( \varrho^{\alpha+1} e^\varrho \frac{d^{k+\alpha}}{d\varrho^{k+\alpha}} \left( e^{-\varrho} \varrho^k \right) \right) = (-1)^{k+\alpha} (k + \alpha)! \left( (k + \alpha + 1)\varrho - k(k + \alpha) \right)$$

It will also be helpful if we recall that the gamma function, as defined below, is related to the factorial for integer values of  $n$ .

$$\Gamma(n + 1) = \int_0^\infty \varrho^n e^{-\varrho} d\varrho = n!$$

This result can easily be obtained by constructing a reduction formula. We can now bring these results together, and after some rearrangement, this yields the final result that

$$C_k^\alpha = \frac{(k + \alpha)!}{k!} (2k + \alpha + 1)$$

As a consequence of the fact that the quantum number  $n$  changes the scaling between  $\varrho$  and  $\rho$ , explicitly proving the orthogonality relation for different values of  $n$  fairly complicated. However, it turns out that it's much easier to manipulate the full radial component of the wave function, defined by

$$R_{n\ell}(\rho) = \sqrt{\frac{8}{n^3} \frac{(n-\ell-1)!}{2n(n+\ell)!}} \left(\frac{2\rho}{n}\right)^\ell L_{n-\ell-1}^{2\ell+1}\left(\frac{2\rho}{n}\right) e^{-\frac{\rho}{n}}$$

which by construction, satisfies the differential equation

$$\frac{1}{\rho^2} \frac{d}{d\rho} \left( \rho^2 \frac{dR_{n\ell}}{d\rho} \right) + \frac{2\rho - \ell(\ell+1)}{\rho^2} R_{n\ell}(\rho) = \frac{R_{n\ell}(\rho)}{n^2}$$

Multiplying this differential equation by  $R_{n'\ell}(\rho)$ , and integrating over all space (with the appropriate factor of  $\rho^2$  to account for the fact that  $\rho$  is a radial coordinate in three dimensional space) gives us

$$\frac{1}{n^2} \int_0^\infty \rho^2 R_{n'\ell}(\rho) R_{n\ell}(\rho) d\rho = \int_0^\infty R_{n'\ell}(\rho) \frac{d}{d\rho} \left( \rho^2 \frac{dR_{n\ell}}{d\rho} \right) + \frac{2\rho - \ell(\ell+1)}{\rho^2} R_{n'\ell}(\rho) R_{n\ell}(\rho) d\rho$$

We can now manipulate the integral on the left hand side in order to obtain a useful result. If we note that, provided  $R_{n\ell}$  is normalisable, the boundary terms at infinity must vanish, we can integrate the first term by parts twice, which leaves us with the expression that

$$\frac{1}{n^2} \int_0^\infty \rho^2 R_{n'\ell}(\rho) R_{n\ell}(\rho) d\rho = \int_0^\infty R_{n\ell}(\rho) \frac{d}{d\rho} \left( \rho^2 \frac{dR_{n'\ell}}{d\rho} \right) + \frac{2\rho - \ell(\ell+1)}{\rho^2} R_{n\ell}(\rho) R_{n'\ell}(\rho) d\rho$$

However, the new integral on the left hand side is just the original integral after swapping the indices  $n$  and  $n'$ . As such, this relationship directly implies that

$$\left( \frac{1}{n^2} - \frac{1}{n'^2} \right) \int_0^\infty \rho^2 R_{n'\ell}(\rho) R_{n\ell}(\rho) d\rho = 0$$

which ensures the orthogonality of the radial functions obtained for different values of  $n$ . Combining this with our earlier result regarding the normalisation of the Laguerre polynomials gives us the complete orthogonality relation

$$\int_0^\infty \rho^2 R_{n'\ell}(\rho) R_{n\ell}(\rho) d\rho = \delta_{nn'}$$

While it is not explicitly useful in our discussion of the hydrogen atom, it is worth commenting on another, much more natural, orthogonality property of the Laguerre polynomials. If we consider the integral

$$D_{kk'}^\alpha = \int_0^\infty \varrho^\alpha e^{-\varrho} L_{k'}^\alpha(\varrho) L_k^\alpha(\varrho) d\varrho$$

then it follows from explicitly substituting in the Rodrigues formula that

$$D_{kk'}^\alpha = \frac{1}{k!k'!} \int_0^\infty \varrho^{-\alpha} e^\varrho \frac{d^{k'}}{d\varrho^{k'}} (e^{-\varrho} \varrho^{k'+\alpha}) \frac{d^k}{d\varrho^k} (e^{-\varrho} \varrho^{k+\alpha}) d\varrho$$

If we assume without loss of generality that  $k \geq k'$ , and integrate by parts  $k$  times, we find that

$$D_{kk'}^\alpha = \frac{1}{k!k'!} \int_0^\infty e^{-\varrho} \varrho^{k+\alpha} \frac{d^k}{d\varrho^k} \left( \varrho^{-\alpha} e^\varrho \frac{d^{k'}}{d\varrho^{k'}} (e^{-\varrho} \varrho^{k'+\alpha}) \right) d\varrho$$

It is quite easy to see that, since we are taking the  $k$ th derivative of a degree  $k'$  polynomial, the integral can only be non zero if  $k = k'$ . In this case, the derivative simply evaluates to  $k!$ , which gives us

$$D_{kk'}^\alpha = \frac{\Gamma(k+\alpha+1)}{k!} \delta_{kk'}$$

## 2.10 Summary

The only thing that remains is for us to bring together all of the disparate parts of our solution, so that we can present them as a single unified result. Firstly, we found that the bound states of a hydrogen like atom are described by three quantum numbers  $n, \ell, m$ , with the energy depending only on  $n$ .

$$E_n = -\frac{Z^2 \mu E_H}{m_e} \frac{1}{2n^2} \quad \begin{array}{l} n = 1, 2, 3, 4, 5, \dots \\ \ell = 0, 1, 2, \dots, n-1 \\ m = -\ell, \dots, 0, \dots, \ell \end{array}$$

This perfectly reproduces Rydberg's formula from earlier. However, it also provides us with much more detailed information about the distribution of these energy levels. We can see that, for given values of  $n$  and  $\ell$ , there are  $2\ell + 1$  states with different values of the magnetic quantum number. Since the angular momentum quantum number can vary between zero and  $n$ , this gives each value of the principle quantum number a total degeneracy of  $n^2$ . This degeneracy is actually very surprising: in nearly all other spherically symmetric potentials the energy depends on the angular momentum quantum number, which gives each level a degeneracy of only  $2\ell + 1$ . This is much less surprising, since the rotation group  $SO(3)$  has irreducible representations of dimension  $2\ell + 1$ . That is to say that the independence of the energy on the magnetic quantum number is a necessary consequence of the symmetry in the potential. The extra 'hidden' symmetry in the Coulomb potential that gives rise to this additional degeneracy is not an exclusively quantum phenomenon. In fact, it is this hidden symmetry which is responsible for the elliptical orbits of planets in a gravitational field, instead of the non-repeating motion that is more common in arbitrary potentials. It is for this reason that even small changes to an atom, which break this extra symmetry, for example adding in multiple electrons, will immediately cause the energy levels to differentiate based on the value of  $\ell$ . This gives rise to the familiar  $S, P, D, F, G$  orbitals of chemistry.

In addition to determining the energy levels, we have also determined the form of the wave functions associated with each state. Combining each of our previous results yields

$$\psi_{n\ell m}(r, \vartheta, \varphi) = \left[ \sqrt{\left(\frac{2\mu Z}{nm_e a_0}\right)^3 \frac{(n-\ell-1)!}{2n(n+\ell)!}} \varrho^\ell L_{n-\ell-1}^{2\ell+1}(\varrho) e^{-\frac{\varrho}{2}} \right] \left[ \sqrt{\frac{(2\ell+1)(\ell-m)!}{4\pi(\ell+m)!}} P_\ell^m(\cos \vartheta) e^{im\varphi} \right]$$

where the scaled radial distance  $\varrho$  is related to the physical distance  $r$  according to the relationship  $\varrho = \frac{2\mu Z r}{nm_e a_0}$ . The special functions that make up this expression are defined by

$$L_k^\alpha(\varrho) = \frac{e^\varrho \varrho^{-\alpha}}{k!} \frac{d^k}{d\varrho^k} (e^{-\varrho} \varrho^{k+\alpha}) \quad P_\ell^m(u) = \frac{(-1)^m}{2^\ell \ell!} (1-u^2)^{\frac{m}{2}} \frac{d^{\ell+m}}{du^{\ell+m}} (u^2-1)^\ell$$

A general property of these wave functions is that they are mutually orthonormal. That is to say that, they obey the orthogonality relation

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} \psi_{n'\ell'm'}^*(r, \vartheta, \varphi) \psi_{n\ell m}(r, \vartheta, \varphi) r^2 \sin \theta d\varphi d\vartheta dr = \delta_{nn'} \delta_{\ell\ell'} \delta_{mm'}$$

which follows directly from the orthogonality relationships we developed for each of the individual components of the wave functions. Importantly, these eigenstates are not complete, that is to say, it is not possible to represent an arbitrary wave function as a linear combination of our bound states. To see this we simply note that, in a complete basis, it must be possible to obtain an arbitrarily good approximation to the Dirac delta function by taking linear combinations of the basis states. Since the delta function has an incredibly large and negative second derivative, the expected value of its energy tends towards infinity; however, since all of our bound states have negative energies, any linear combination of them must have a negative expected energy. Really this should not be surprising, we would expect the discrete bound states of the atom to transition into a continuous spectrum once the electron has enough energy to escape the nucleus's potential well.



## 3 The Operator Approach

### 3.1 Linear Operators

While the wave mechanical approach of solving partial differential equations is a perfectly valid treatment of the hydrogen atom, it can often be useful to analyse quantum systems in a more abstract way using operator methods, since this can often make it easier to obtain key results of interest.

When working with abstract operators we denote the state of a system not with a wave function, but instead with a state vector, referred to as a ket and denoted by  $|\psi\rangle$ . Kets are elements of the (typically infinite dimensional) vector space defined by all possible states of the system. In fact, this vector space contains more than just all possible states of the system since it also contains entities like  $2|\psi\rangle$ , which are not physically distinct states. Thus, the physical states of the system are those kets who have a unit norm, where the norm is defined by the inner product of a ket with itself, as shown below.

$$\| |\psi\rangle \|^2 = \langle \psi, \psi \rangle$$

In the wave mechanical view this inner product is represented by the overlap integral of two wave functions, and so the restriction of physical states to kets of unit norm is equivalent to the restriction that the probability distribution of the system must be normalised. This inner product must obey certain special properties. Firstly, it must have a conjugate symmetry between its two arguments, meaning that

$$\langle \phi, \psi \rangle = \langle \psi, \phi \rangle^*$$

Secondly, it must be linear in the rightmost argument, giving the result that, for arbitrary complex numbers  $a$  and  $b$

$$\langle \phi, a\psi + b\chi \rangle = a\langle \phi, \psi \rangle + b\langle \phi, \chi \rangle$$

Finally, the inner product must be positive definite, meaning that for arbitrary  $\psi$

$$\langle \psi, \psi \rangle \geq 0$$

with equality if, and only if,  $|\psi\rangle$  is the unique zero ket, which is defined as the identity element of addition. For every ket  $|\psi\rangle$ , we can use the inner product to define a linear functional  $\langle \psi|$ , called a bra, which acts as a linear mapping between the space of kets and the complex numbers, according to the rule

$$\langle \psi|\phi \rangle = \langle \psi, \phi \rangle$$

for arbitrary  $|\phi\rangle$ . We can then identify a linear operator  $\hat{O}$  as a linear mapping between different kets. That is to say that it maps  $|\psi\rangle$  onto  $\hat{O}|\psi\rangle$ , subject to the restriction that

$$\hat{O}(a|\psi\rangle + b|\chi\rangle) = a\hat{O}|\psi\rangle + b\hat{O}|\chi\rangle$$

for any complex numbers  $a$  and  $b$ . For every operator  $\hat{O}$ , we can define a second operator, known as the adjoint operator,  $\hat{O}^\dagger$ , which has the property that

$$\langle \phi|\hat{O}|\psi\rangle = \langle \psi|\hat{O}^\dagger|\phi\rangle^*$$

for all possible bras and kets. We can define operator addition and multiplication in a natural way, using the rules that, for any two operators  $\hat{O}$  and  $\hat{Q}$

$$(\hat{O} + \hat{Q})|\psi\rangle = \hat{O}|\psi\rangle + \hat{Q}|\psi\rangle \qquad (\hat{O}\hat{Q})|\psi\rangle = \hat{O}(\hat{Q}|\psi\rangle)$$

An immediate consequence of this definition is that operator multiplication is associative (in essence, this is the definition); however, one thing that it is certainly not is commutative. This leads us to define the commutator  $[\hat{O}, \hat{Q}]$ , and, for completeness, the anticommutator  $\{\hat{O}, \hat{Q}\}$  according to rules that

$$[\hat{O}, \hat{Q}] = \hat{O}\hat{Q} - \hat{Q}\hat{O} \qquad \{\hat{O}, \hat{Q}\} = \hat{O}\hat{Q} + \hat{Q}\hat{O}$$

Based on these definitions, we can identify four classes of special operators, which have a lot of useful properties. Hermitian operators are those that are self adjoint, whereas anti-Hermitian operators are equal to minus their own adjoint. Unitary operators have the property that their adjoint is also their inverse (the inverse of the operator  $\hat{O}$  is simply the operator that maps  $\hat{O}|\psi\rangle$  onto  $|\psi\rangle$ ). All of these classes are special cases of the more general normal operators, those operators that commute with their adjoint. In summary, if  $\hat{H}$  is Hermitian,  $\hat{A}$  is anti-Hermitian,  $\hat{U}$  is unitary, and  $\hat{N}$  is normal, we must have

$$\hat{H} = \hat{H}^\dagger \quad \hat{A} = -\hat{A}^\dagger \quad \hat{U}^\dagger \hat{U} = 1 \quad [\hat{N}, \hat{N}^\dagger] = 0$$

These operators have a number of special properties which make them useful things to consider. We shall derive the general properties of a normal operator, and then, where appropriate, discuss the special cases as they arise. Starting from the definition of a normal operator, it immediately follows that, for any ket  $|\psi\rangle$

$$\langle\psi|\hat{N}^\dagger\hat{N} - \hat{N}\hat{N}^\dagger|\psi\rangle = \|\hat{N}|\psi\rangle\|^2 - \|\hat{N}^\dagger|\psi\rangle\|^2 = 0$$

Before we go on to discuss the any more properties of normal operators, we should take a brief moment to define the notion of eigenstates and eigenvalues. A ket  $|\psi_\lambda\rangle$  is referred to as an eigenstate of the operator  $\hat{O}$ , if it satisfies the eigenvalue equation

$$\hat{O}|\psi_\lambda\rangle = \lambda|\psi_\lambda\rangle$$

where  $\lambda$  is some complex number, referred to as the eigenvalue of  $|\psi_\lambda\rangle$ . If we consider the case when  $|\psi_\lambda\rangle$  is an eigenstate of a normal operator, then it follows that we must have

$$\hat{N}|\psi_\lambda\rangle = \lambda|\psi_\lambda\rangle \implies \langle\psi_\lambda|\hat{N}^\dagger|\psi_\lambda\rangle = \langle\psi_\lambda|\hat{N}|\psi_\lambda\rangle^* = \lambda^* \|\psi_\lambda\|^2$$

This implies that it must be possible to write  $\hat{N}^\dagger|\psi_\lambda\rangle$  in the form

$$\hat{N}^\dagger|\psi_\lambda\rangle = \lambda^*|\psi_\lambda\rangle + |\chi\rangle$$

where  $\langle\psi_\lambda|\chi\rangle = 0$ . If we now evaluate the norm of  $\hat{N}^\dagger|\psi_\lambda\rangle$ , we find that

$$\|\hat{N}^\dagger|\psi_\lambda\rangle\|^2 = |\lambda|^2\|\psi_\lambda\|^2 + \|\chi\|^2 = \|\hat{N}|\psi_\lambda\rangle\|^2 + \|\chi\|^2$$

Given our previous result about the interaction of a normal operator with the norm of a ket, we can conclude that  $|\chi\rangle$  must have norm zero, and hence must be equal to the zero ket. Thus, we can conclude that

$$\hat{N}^\dagger|\psi_\lambda\rangle = \lambda^*|\psi_\lambda\rangle$$

In other words, if  $|\psi_\lambda\rangle$  is an eigenstate of  $\hat{N}$ , with eigenvalue  $\lambda$ , then it will also be an eigenstate of  $\hat{N}^\dagger$  with eigenvalue  $\lambda^*$ . This result immediately implies that the eigenvalues of a Hermitian operator are real, the eigenvalues of an anti-Hermitian operator are imaginary, and the eigenvalues of a unitary operator have modulus one. This result then allows us to deduce another very useful property of normal operators. Let us consider two distinct eigenstates of  $\hat{N}$ ,  $|\psi_\lambda\rangle$  and  $|\psi_\mu\rangle$ . Then we can say that

$$\langle\psi_\mu|\hat{N}|\psi_\lambda\rangle = \lambda\langle\psi_\mu|\psi_\lambda\rangle = \langle\psi_\lambda|\hat{N}^\dagger|\psi_\mu\rangle^* = (\mu^*\langle\psi_\lambda|\psi_\mu\rangle)^* = \mu\langle\psi_\mu|\psi_\lambda\rangle$$

This implies that

$$(\lambda - \mu)\langle\psi_\mu|\psi_\lambda\rangle = 0$$

which means that, provided the eigenvalues  $\lambda$  and  $\mu$  are different, the eigenstates must be orthogonal to one another. In the case of a degenerate eigenvalue, it follows from linearity that any linear combination of the degenerate eigenstates will also be an eigenstate of the same eigenvalue. Thus, we can always use the Gram-Schmidt procedure to obtain an orthogonal basis that spans the eigenspace.

### 3.2 The Hamiltonian

It is a fundamental postulate of quantum mechanics that, observable quantities are represented by Hermitian operators on the space of all possible states. If the operator  $\hat{A}^*$  represents some observable, then there exists some probability distribution for the different values that observable could take when measured. The moments of this probability distribution can be calculated by evaluating

$$\langle \hat{A}^n \rangle = \langle \psi | \hat{A}^n | \psi \rangle$$

where  $\langle \hat{A}^n \rangle$  is the  $n$ th moment of the probability distribution, and  $|\psi\rangle$  is the state of the system before the measurement. Formally, this allows us to write

$$\hat{A}|\psi\rangle = \langle \hat{A} | \psi \rangle + |\chi\rangle$$

where  $\langle \psi | \chi \rangle = 0$ . We can define the variance in the measurements just as we would do for classical statistics, which yields the result

$$\sigma_{\hat{A}}^2 = \langle (\hat{A} - \langle \hat{A} \rangle)^2 \rangle = \langle \psi | \hat{A}^2 | \psi \rangle - \langle \hat{A} \rangle^2$$

where we have used the fact that the zeroth moment of any probability distribution, which is just the expected value of one, is unity to say that  $\langle \psi | \psi \rangle = 1$ . Utilising the fact that  $\hat{A}$  is Hermitian, we can rewrite this as

$$\sigma_{\hat{A}}^2 = \langle \hat{A} \psi | \hat{A} \psi \rangle - \langle \hat{A} \rangle^2 = \langle \chi | \chi \rangle$$

Thus, it follows that, if the system is in a state  $|A\rangle$  for which this observable has a definite value  $A$ , we must have

$$\sigma_{\hat{A}}^2 = 0 \implies |\chi\rangle = 0 \implies \hat{A}|A\rangle = A|A\rangle$$

In other words, states in which a given observable has a definite value correspond to eigenstates of the appropriate operator, with the values of the observable being equal to the eigenvalues.

The operator representing the total energy of a system is referred to as the Hamiltonian, and is denoted by  $\hat{H}$ . The time independent Schrödinger equation is simply the eigenvalue equation of the Hamiltonian

$$\hat{H}|\psi\rangle = E|\psi\rangle$$

Solving this equation amounts to finding the eigenvalues of the Hamiltonian, and hence determining the allowed energies of the system. In the case of a hydrogen like atom, the Hamiltonian takes the form

$$\hat{H} = \frac{1}{2\mu} (\hat{p}_r^2 + \hat{r}^{-2} \hat{L}^2) - \frac{Ze^2}{4\pi\epsilon_0} \hat{r}^{-1}$$

where  $\hat{r}$ ,  $\hat{p}_r$ , and  $\hat{L}^2$  are Hermitian operators representing the electron's radial distance from the nucleus, radial momentum, and angular momentum, all of which we shall define formally later. Raising an operator to a negative power can be understood as inverting the operator, that is to say  $\hat{r}^{-1}$  is the operator defined such that

$$\hat{r} \hat{r}^{-1} = \hat{r}^{-1} \hat{r} = 1$$

Perhaps unsurprisingly, this Hamiltonian can be generalised for a particle moving in an arbitrary spherically symmetric potential

$$\hat{H} = \frac{1}{2\mu} (\hat{p}_r^2 + \hat{r}^{-2} \hat{L}^2) + U(\hat{r})$$

where the function of the radial operator  $U(\hat{r})$  is defined by replacing  $r$  with  $\hat{r}$  in the power series expansion of the classical expression for the potential  $U(r)$ .

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\*Not to be confused with the previous section where  $\hat{A}$  was an anti-Hermitian operator

### 3.3 Position and Momentum

In three dimensions the position of a particle is represented by three independent coordinates. Quantum mechanically this means that we have three mutually commuting position operators, which we shall denote by  $\hat{r}_i$ , with the index  $i$  taking values from 1 to 3. The commutation relation is simply

$$[\hat{r}_i, \hat{r}_j] = 0$$

We then define the conjugate momentum operators  $\hat{p}_i$  to be the generators of motion along each of these coordinate directions. That is to say, we want  $\hat{p}_i$  to be the operator such that

$$e^{\frac{i\xi_j \hat{p}_j}{\hbar}} \hat{r}_i e^{-\frac{i\xi_j \hat{p}_j}{\hbar}} = \hat{r}_i + \xi_i$$

where the components  $\xi_j$  represent some constant displacement. This is equivalent to saying that the operator

$$\hat{T} = e^{-\frac{i\xi_j \hat{p}_j}{\hbar}} = \sum_{n=0}^{\infty} \frac{(-i)^n (\xi_j \hat{p}_j)^n}{\hbar^n n!} = 1 - \frac{i\xi_j \hat{p}_j}{\hbar} - \frac{\xi_j^2 \hat{p}_j^2}{2\hbar^2} + \dots$$

acts on a state by translating it through the displacement  $x_i$ . Since the position operators are all independent, we would like translations to be decomposable by their coordinates. This imposes the restriction that the momentum operators must all commute with one another. That is to say

$$e^{-\frac{i\xi_j \hat{p}_j}{\hbar}} = e^{-\frac{i\xi_1 \hat{p}_1}{\hbar}} e^{-\frac{i\xi_2 \hat{p}_2}{\hbar}} e^{-\frac{i\xi_3 \hat{p}_3}{\hbar}} \implies [\hat{p}_i, \hat{p}_j] = 0$$

This condition leads to the result that  $\hat{T}$  is unitary, as can easily be seen by writing out the series expansion for  $\hat{T}^\dagger \hat{T}$ . Thus, it follows that our definition of the momentum operators is equivalent to requiring that

$$[\hat{r}_i, \hat{T}] = \xi_i \hat{T}$$

This implies that the commutation relation between position and momentum must take the form

$$[\hat{r}_i, \hat{p}_j] = i\hbar \delta_{ij}$$

This result, known as the canonical commutation relation, is one of the most important, and most fundamental in quantum mechanics. As it happens, this is still only enough to determine the momentum operators up to arbitrary additive constants, which makes sense since altering these constants would simply correspond to changing between inertial reference frames. Furthermore, it follows directly from this commutation relation that the position operators act as the generators of these shifts. This means that

$$e^{-\frac{i\eta_j \hat{p}_j}{\hbar}} \hat{p}_i e^{\frac{i\eta_j \hat{p}_j}{\hbar}} = \hat{p}_i + \eta_i$$

We can now define the radial distance operator  $\hat{r}$  in terms of the position operators, in exactly the same way as we would classically

$$\hat{r} = \sqrt{\hat{r}_i \hat{r}_i} = \sqrt{\hat{r}_1 \hat{r}_1 + \hat{r}_2 \hat{r}_2 + \hat{r}_3 \hat{r}_3}$$

It can also be useful to define the direction operators

$$\hat{n}_i = \hat{r}_i \hat{r}^{-1}$$

which measure the direction of the particle's position, relative to the origin. Classically, we would expect the radial component of the total momentum to be given by  $\hat{n}_i \hat{p}_i$ ; however, due to the non-commutativity of the operators, this new operator is not Hermitian. The way around this is to make use of the anticommutator

$$\hat{p}_r = \frac{1}{2} \{\hat{n}_i, \hat{p}_i\} = \frac{\hat{n}_i \hat{p}_i + \hat{p}_i \hat{n}_i}{2}$$

Using the canonical commutation relation, we can derive several other useful commutation relations

$$[\hat{r}, \hat{p}_i] = i\hbar \hat{n}_i \qquad [\hat{n}_i, \hat{p}_j] = i\hbar (\delta_{ij} - \hat{n}_i \hat{n}_j) \hat{r}^{-1}$$

With these results we can confirm that, as we might have expected  $[\hat{r}, \hat{p}_r] = i\hbar$ .

### 3.4 Angular Momentum

In the same way as we defined momentum to be the generator of linear translations, we define angular momentum to be the generator of rotations. In particular, we can identify the Hermitian operator  $\hat{L}_3$ , which generates rotations about the  $z$  axis. As such, we must have the relations

$$e^{\frac{i\varphi\hat{L}_3}{\hbar}}\hat{r}_1e^{-\frac{i\varphi\hat{L}_3}{\hbar}} = \cos\varphi\hat{r}_1 - \sin\varphi\hat{r}_2 \quad e^{\frac{i\varphi\hat{L}_3}{\hbar}}\hat{r}_2e^{-\frac{i\varphi\hat{L}_3}{\hbar}} = \cos\varphi\hat{r}_2 + \sin\varphi\hat{r}_1$$

as well as the trivial fact that, since rotations about the  $z$  axis can not affect the  $z$  particle's  $z$  coordinate, we must have  $[r_3, \hat{L}_3] = 0$ . Since the rotation operator is unitary, we can note that these conditions simplify down to give

$$\left[\hat{r}_1, e^{-\frac{i\varphi\hat{L}_3}{\hbar}}\right] = e^{-\frac{i\varphi\hat{L}_3}{\hbar}}\left((\cos\varphi - 1)\hat{r}_1 - \sin\varphi\hat{r}_2\right) \quad \left[\hat{r}_2, e^{-\frac{i\varphi\hat{L}_3}{\hbar}}\right] = e^{-\frac{i\varphi\hat{L}_3}{\hbar}}\left((\cos\varphi - 1)\hat{r}_2 + \sin\varphi\hat{r}_1\right)$$

These relationships can be obtained with the fundamental commutation relations

$$[\hat{r}_1, \hat{L}_3] = -i\hbar\hat{r}_2 \quad [\hat{r}_2, \hat{L}_3] = i\hbar\hat{r}_1 \quad [\hat{r}_3, \hat{L}_3] = 0$$

Moreover, by cyclically permuting the indices we can deduce that, the general commutation relation between position and angular momentum takes the form

$$[\hat{r}_i, \hat{L}_j] = i\hbar\varepsilon_{ijk}\hat{r}_k$$

where  $\varepsilon_{ijk}$  is the Levi-Civita symbol. In fact, this result applies to any set of three operators that represent the components of a vector. This is precisely because the definition of a vector is an object whose components transform in the same way as the components of position, under rotations. Thus, we can say that, if the operators  $\hat{v}_i$  are the components of some vector observable, they must obey

$$[\hat{v}_i, \hat{L}_j] = i\hbar\varepsilon_{ijk}\hat{v}_k$$

Since this is true for all vector operators, it must hold true for the angular momentum operators themselves. This commutation relation defines the algebra of quantum mechanical angular momentum, and as such it is vitally important.

$$[\hat{L}_i, \hat{L}_j] = i\hbar\varepsilon_{ijk}\hat{L}_k$$

It makes sense that the components of the angular momentum do not commute with one another, since unlike translations, rotations are not commutative. Thus, as the generators of rotations, we would not expect the angular momentum operators to be commutative. Just as we can in classical mechanics, we can express the angular momentum in terms of the position and momentum operators.

$$\hat{L}_i = \varepsilon_{ijk}\hat{r}_j\hat{p}_k$$

It can be easily verified from the canonical commutation relation that these operators have all of the desired properties. Another useful operator for us to define is the total angular momentum operator  $\hat{L}^2$ , which is given by

$$\hat{L}^2 = \hat{L}_i\hat{L}_i = \hat{L}_1\hat{L}_1 + \hat{L}_2\hat{L}_2 + \hat{L}_3\hat{L}_3$$

If we consider the commutation of an arbitrary vector operator  $\hat{v}_i$  with the total angular momentum, we find that

$$[\hat{v}_i, \hat{L}] = [\hat{v}_i, \hat{L}_j\hat{L}_j] = [\hat{V}_i, \hat{L}_j]\hat{L}_j + \hat{L}_j[\hat{v}_i, \hat{L}_j]$$

where the last equality follows by simply expanding out the commutators. We can then substitute in our general result for the commutation relation, which yields

$$[\hat{v}_i, \hat{L}^2] = i\hbar\varepsilon_{ijk}\{\hat{L}_j, \hat{v}_k\}$$

It immediately follows from this result that any of the individual components of the angular momentum must commute with the total angular momentum, since if  $\hat{v}_k = \hat{L}_k$  then the anticommutator becomes symmetric in the indices  $j$  and  $k$ , which cancels with the antisymmetry of the Levi-Civita symbol to give zero. This result has the perhaps unsurprising consequence that rotations in space do not affect the magnitude of a system's angular momentum.

Given any two commuting Hermitian operators, it is always possible to find a set of orthonormal kets, such that each ket is an eigenstate of both operators. By convention, we describe a system's angular momentum state in terms of the total magnitude of the angular momentum and its projection along the  $z$  axis. That is to say, we choose as our basis kets eigenstates of both  $\hat{L}_3$  and  $\hat{L}^2$ . It becomes convenient for us to define two new operators

$$\hat{L}_{\pm} = \hat{L}_{\mp}^{\dagger} = \hat{L}_1 \pm i\hat{L}_2$$

A trivial application of the angular momentum commutation relation shows that these operators possess the remarkably useful property that

$$[\hat{L}^2, \hat{L}_{\pm}] = 0 \qquad [\hat{L}_3, \hat{L}_{\pm}] = \pm\hbar\hat{L}_{\pm}$$

This means that, if  $|m\rangle$  is an eigenstate of  $\hat{L}_3$  with eigenvalue  $m\hbar$ , then we must have

$$\hat{L}_3\hat{L}_{\pm}|m\rangle = (\hat{L}_{\pm}\hat{L}_3 \pm \hbar\hat{L}_{\pm})|m\rangle = (m \pm 1)\hbar\hat{L}_{\pm}|m\rangle$$

In other words  $\hat{L}_{\pm}|m\rangle$  is also an eigenstate, with an eigenvalue that is either higher or lower by  $\hbar$ . It is for this reason that  $\hat{L}_+$  is known as the raising operator, while  $\hat{L}_-$  is called the lowering operator. The immediate question we should ask is if there is any limit on this raising and lowering of the eigenvalues. To find the limit we can note that for arbitrary  $|\psi\rangle$

$$\langle \hat{L}_+\psi | \hat{L}_+\psi \rangle = \langle \psi | \hat{L}_-\hat{L}_+ | \psi \rangle = \langle \psi | \hat{L}^2 - \hat{L}_3^2 - \hbar\hat{L}_3 | \psi \rangle \geq 0$$

Clearly, since the raising operator commutes with  $\hat{L}^2$ , if we keep raising the eigenvalue indefinitely, this inner product will eventually become negative. The only way to prevent this is if there exists some maximal value of  $m$  whose eigenstate is mapped onto the zero ket by the raising operator. If we denote by  $|\ell, m\rangle$  a state whose total angular momentum is such that this maximal value of  $m$  is  $\ell$ , with a  $z$  component of  $m\hbar$ , then it follows that we must have

$$\langle \ell, \ell | \hat{L}_-\hat{L}_+ | \ell, \ell \rangle = \langle \ell, \ell | \hat{L}^2 - \hat{L}_3^2 - \hbar\hat{L}_3 | \ell, \ell \rangle = \langle \ell, \ell | \hat{L}^2 - \hbar^2\ell(\ell+1) | \ell, \ell \rangle = 0$$

This then directly implies that we must have

$$\hat{L}^2 | \ell, m \rangle = \hbar^2\ell(\ell+1) | \ell, m \rangle$$

Repeating this argument for the lowering operator, we can deduce that the minimal value of  $m$  must be  $-\ell$ . However, in order for these states to actually block the ladder operators from indefinite raising/lowering, it needs to be the case that every possible state can be obtained by repeated application of the ladder operators to the boundary states. Thus, the magnetic quantum number  $m$  can only increase in integer steps. This means that  $2\ell$  must be an integer, so that the two boundary states are connected by an integer number of steps. We can note that, if  $\ell$  is half integer, then so too is  $m$ , which based on our definition of angular momentum as the generator of rotations, means that the state acquires a factor of  $-1$  when rotated through  $2\pi$  radians. For certain types of angular momentum, known as spin or intrinsic angular momentum, this does not present a problem; however, in the case of orbital angular momentum, which corresponds to the physical motion of a particle, we must further restrict  $\ell$  to take integer values. Thus, the orbital angular momentum eigenstates take the form

$$\begin{aligned} \hat{L}_3 | \ell, m \rangle &= m\hbar | \ell, m \rangle & \ell &= 0, 1, 2, 3, \dots \\ \hat{L}^2 | \ell, m \rangle &= \hbar^2\ell(\ell+1) | \ell, m \rangle & m &= -\ell, \dots, \ell \end{aligned}$$

We can recognise these quantum numbers as the same as those that we used to describe the spherical harmonics; however, now we have a much more sophisticated understanding of where the quantisation comes from, as opposed to just fixing the values in order to make an equation work.

So far, our discussion of angular momentum has been very general, and would apply to any system characterised by the same commutation relations. In the case of a single particle's orbital angular momentum, it is possible for us to take our operator analysis even further, by constructing raising and lowering operators for the angular momentum quantum number. However, before we do this, let us construct the operator  $\hat{l}$ , which has the property that

$$\hat{l}|\ell, m\rangle = \ell|\ell, m\rangle$$

It follows from simple manipulation that this operator is given by the expression

$$\hat{l} = \frac{\sqrt{4\hat{L}^2 + \hbar^2} - \hbar}{2\hbar}$$

where the function of an operator is to be understood in the usual sense. We can now define the vector operator  $\hat{R}_i$  to be given by

$$\hat{R}_i = \frac{i}{\hbar}\varepsilon_{ijk}\hat{n}_j\hat{L}_k + \hat{n}_i(\hat{l} + 1)$$

Verifying that this is indeed a vector operator simply requires us to substitute in the rotation transformations for each of the individual components, and then note that this gives the desired result for the overall operator. Since  $\hat{R}_i$  is a vector operator, we can immediately say that

$$[\hat{L}^2, \hat{R}_i] = -i\hbar\varepsilon_{ijk}\{\hat{L}_j, \hat{R}_k\} = 2i\hbar\varepsilon_{ijk}\hat{R}_j\hat{L}_k + 2\hbar^2\hat{R}_i$$

where in the last step we have simply used the commutator to swap the order of one of the terms in the anticommutator, and relabelled the indices in the first term for convenience. If we now expand the first term we find that

$$i\hbar\varepsilon_{ijk}\hat{R}_j\hat{L}_k = \varepsilon_{ijk}\varepsilon_{ljm}\hat{n}_l\hat{L}_m\hat{L}_k + i\hbar\varepsilon_{ijk}\hat{n}_j\hat{L}_k(\hat{l} + 1)$$

where we have used the fact that  $\hat{L}_i$  must commute with  $\hat{l}$  to rewrite the last term slightly. We can expand out the first term using the result that

$$\varepsilon_{ijk}\varepsilon_{ljm} = \delta_{il}\delta_{km} - \delta_{im}\delta_{kl}$$

Noting that  $\hat{n}_i\hat{L}_i = 0$  and using the angular momentum commutator to rearrange the second term into this form, we obtain

$$\varepsilon_{ijk}\varepsilon_{ljm}\hat{n}_l\hat{L}_m\hat{L}_k = \hat{n}_i\hat{L}^2 - \hat{n}_k\hat{L}_i\hat{L}_k = \hat{n}_i\hat{L}^2 - i\hbar\varepsilon_{ijk}\hat{n}_j\hat{L}_k$$

Substituting this back into the original expression, we find that we have

$$i\hbar\varepsilon_{ijk}\hat{R}_j\hat{L}_k = \hat{n}_i\hat{L}^2 + i\hbar\varepsilon_{ijk}\hat{n}_j\hat{L}_k\hat{l} = \hbar^2\hat{R}_i\ell + \hat{n}_i(\hat{L}^2 - \hat{l}(\hat{l} + 1)) = \hbar^2\hat{R}_i\hat{l}$$

Putting this all together, we find that we have the commutation relation

$$[\hat{L}^2, \hat{R}_i] = 2\hbar^2\hat{R}_i(\hat{l} + 1)$$

which we can see will lead to any component of  $\hat{R}_i$  raising the angular momentum quantum number by one. Of particular interest is  $\hat{R}_3$ , since it commutes with  $\hat{L}_3$ , and hence does not change the value of the magnetic quantum number. The construction of the lowering operator  $\hat{S}_i$  is essentially the same, taking the form

$$\hat{S}_i = \frac{i}{\hbar}\varepsilon_{ijk}\hat{n}_j\hat{L}_k - \hat{n}_i\hat{l} \implies [\hat{L}^2, \hat{S}_i] = -2\hbar^2\hat{S}_i\hat{l}$$

It is thus possible, at least in principle, for us to write any angular momentum state as the result of operators acting on the  $|0, 0\rangle$  state.

$$|\ell, \pm m\rangle = \alpha\hat{L}_\pm^m\hat{R}_3^\ell|0, 0\rangle$$

where  $\alpha$  is a normalisation constant.

### 3.5 The Energy Spectrum

Let us now return to the Hamiltonian of a hydrogen like atom

$$\hat{H} = \frac{1}{2\mu} \left( \hat{p}_r^2 + \hat{r}^{-2} \hat{L}^2 \right) - \frac{Ze^2}{4\pi\epsilon_0} \hat{r}^{-1}$$

The key commutation relations for this problem are

$$[\hat{r}, \hat{L}_i] = 0 \qquad [\hat{p}_r, \hat{L}_i] = 0 \qquad [\hat{r}, \hat{p}_r] = i\hbar$$

Since the Hamiltonian commutes with the angular momentum, it must be possible to choose a basis of energy eigenstates that are also eigenstates of both  $\hat{L}^2$  and  $\hat{L}_3$ . Furthermore, since the ladder operators  $\hat{L}_\pm$  commute with the Hamiltonian, the energy must not depend on the magnetic quantum number. In order to deal with the angular momentum quantum number, it is convenient for us to introduce the operator

$$\hat{A} = \frac{a}{\sqrt{2}} \left( \frac{i\hat{p}_r}{\hbar} - \frac{\hat{l} + 1}{\hat{r}} + \frac{1}{a(\hat{l} + 1)} \right)$$

where  $a = \frac{\hbar^2 4\pi\epsilon_0}{Z\mu e^2} = \frac{m_e a_0}{Z\mu}$  is the scaled Bohr radius. Expressing the Hamiltonian in terms of this operator yields the result that

$$\hat{H} = \frac{\hbar^2}{\mu a^2} \left( \hat{A}^\dagger \hat{A} - \frac{1}{2(\hat{l} + 1)^2} \right)$$

We can also calculate the commutator of  $\hat{A}$  with its adjoint, which yields the result that

$$[\hat{A}, \hat{A}^\dagger] = \frac{a^2(\hat{l} + 1)}{\hat{r}^2}$$

From here it is fairly straightforward to calculate the commutator of  $\hat{A}$  with the Hamiltonian, which gives us

$$[\hat{H}, \hat{A}] = -\frac{\hbar^2(\hat{l} + 1)}{\mu \hat{r}^2} \hat{A}$$

The value in this result becomes immediately apparent once we realise the similarities between this result and

$$[\hat{H}, \hat{R}_i] = \hat{R}_i \frac{\hbar^2(\hat{l} + 1)}{\mu \hat{r}^2}$$

. This allows us to deduce that

$$[\hat{H}, \hat{R}_i \hat{A}] = [\hat{H}, \hat{R}_i] \hat{A} + \hat{R}_i [\hat{H}, \hat{A}] = \hat{R}_i \frac{\hbar^2(\hat{l} + 1)}{\mu \hat{r}^2} \hat{A} - \hat{R}_i \frac{\hbar^2(\hat{l} + 1)}{\mu \hat{r}^2} \hat{A} = 0$$

Furthermore, since  $\hat{A}$  commutes with every component of the angular momentum, this means that the operator  $\hat{R}_3 \hat{A}$  acts as a raising operator for the angular momentum quantum number, without changing the total energy of the particle, or the magnetic quantum number. Although it is less important for our argument, it is possible to construct a lowering operator from  $\hat{S}_3$  and the operator

$$\hat{B} = \frac{a}{\sqrt{2}} \left( -\frac{i\hat{p}_r}{\hbar} - \frac{\hat{l}}{\hat{r}} + \frac{1}{a\hat{l}} \right)$$

which is essentially just a repetition of the raising operator's derivation. The commutation of these additional ladder operators with the Hamiltonian is a consequence of the 'hidden' symmetry present in the Coulomb potential that we discussed earlier. The existence of these operators essentially decouples the energy from the angular momentum in a hydrogen like atom.



To determine the energies of the bound states we simply note that, as per the definition of the inner product, we must have

$$\langle E, \ell, m | \hat{A}^\dagger \hat{A} | E, \ell, m \rangle = \langle E, \ell, m | \left( \frac{\mu a^2 \hat{H}}{\hbar^2} + \frac{1}{2(\hat{l} + 1)^2} \right) | E, \ell, m \rangle = \frac{\mu a^2 E}{\hbar^2} + \frac{1}{2(\ell + 1)^2} \geq 0$$

Since in a bound state  $E < 0$ , each energy level has an upper bound on the allowed values of the angular momentum quantum number. Just as we saw with angular momentum, the only way for a raising operator to be consistent with an upper limit is if there exists a state that is mapped to the zero ket by the raising operator. This implies that there exists an integer  $n$  (which is equal to the largest possible value of  $\ell$  plus one) such that

$$E = -\frac{\hbar^2}{\mu a^2} \frac{1}{2n^2} = -\frac{Z^2 \mu E_H}{m_e} \frac{1}{2n^2}$$

Starting from the state  $|E, n-1, 0\rangle$ , we can generate all  $n^2$  of the degenerate states by repeatedly applying the operators  $\hat{S}_3 \hat{B}$  and  $\hat{L}_\pm$ .