QUANTUM MECHANICS A (SPA-5319)

The Hydrogen Atom and Angular Momentum

In order to solve the Hydrogen atom quantum mechanically we shall assume that the atom consists of a proton that is stationary and at the origin (we are neglecting the centre of mass motion of the atom). The potential that the electron experiences is a simple electrostatic, time-independent and radial potential. The natural coordinate system to use is therefore a spherical polar coordinate system (see figure 1).

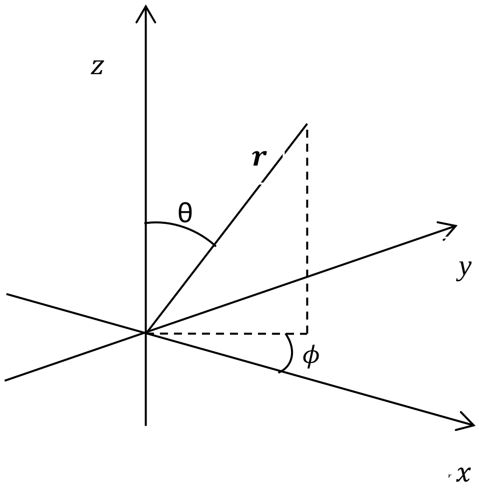
proton – At origin and stationary

1 – Orbiting electron

V – Time independent

Simple Electrostatic potential

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



$$0 \le \theta \le \pi$$

$$0 \le \varphi \le 2\pi$$

$$0 \le r \le \infty$$

Figure 1: *Spherical polar coordinates, used throughout this section.*

Our initial approach is to consider the Time Independent Schrödinger Equation (TISE) in three dimensions. We have already encountered this in Cartesian form:

$$\frac{-\hbar^2}{2m}\nabla^2\psi(\mathrm{x,y,z}) + \mathrm{V}\psi(\mathrm{x,y,z}) = \mathrm{E}\psi(\mathrm{x,y,z})$$

where:

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

Clearly for the Hydrogen atom we will require the time-independent Schrödinger equation in polar form. The first point to consider is how to write the gradient squared in polar form. I have taken this from the literature, but a general method for converting spatial derivatives from one coordinate system to another can be found in M. L. Boas , Mathematical Methods in the Physical Sciences, Wiley, ISBN -13 978-0-471-19826-0.

In any case, using the fact that

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2 sin\theta}\frac{\partial\left(sin\theta\frac{\partial}{\partial\theta}\right)}{\partial\theta} + \frac{1}{r^2 sin^2\theta}\frac{\partial^2}{\partial\varphi^2}$$

we can rewrite the time-independent Schrödinger equation for use with a spherical polar wavefunction, $\psi(\mathrm{r}, \theta, \varphi)$, in the following form:

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

As the potential is radial (and we are not concerning ourselves with the actual form of the potential at this point) we can proceed using the technique of separation of variables. Thus we can write the wavefunction as the product of a radial and an angular component:

$$\psi(r,\theta,\varphi) = R(r)Y(\theta,\varphi) = RY$$

Substituting these into the time-independent Schrödinger equation we obtain

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

On the left-hand side are all functions of *r* and on the right-hand side all functions of θ and φ. In order for these to be true for any values of any variables, the two sides must equal a constant, C_1. I shall write this constant as $C_1 = l(l+1)$, where, for the time being, l can be taken to be any complex number, although its significance will become apparent in due course.

We can now write the original Schrödinger equation as two equations, one radial and one angular:

$$\frac{1}{R}\frac{\partial\left(r^2\frac{\partial R}{\partial r}\right)}{\partial r} - \frac{2mr^2}{\hbar^2}(V-E) = l(l+1)$$

and

$$\frac{-1}{Y}\left\{\frac{1}{sin\theta}\frac{\partial\left(sin\theta\frac{\partial Y}{\partial\theta}\right)}{\partial\theta} + \frac{1}{sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2}\right\} = l(l+1)$$

We shall now concentrate on the angular equation and apply separation of variables once again:

$$Y(\theta,\varphi) = \Theta(\theta)\Phi(\varphi) = \Theta\Phi$$

We substitute this into

$$\frac{-1}{Y}\left\{\frac{1}{sin\theta}\frac{\partial\left(sin\theta\frac{\partial Y}{\partial\theta}\right)}{\partial\theta}+\frac{1}{sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2}\right\}=l(l+1)$$

to obtain

$$-\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\varphi^2}=\frac{sin\theta}{\Theta}\frac{\partial\left(sin\theta\frac{\partial\Theta}{\partial\theta}\right)}{\partial\theta}+l(l+1)sin^2\theta$$

Once again these must be equal to a constant, C_2, which I shall write as $C_2 = m_l^2$. For the time being, m_l can be taken as any complex number, although we shall see it is much simpler than that.

Our two equations thus become:

$$\frac{sin\theta}{\Theta}\frac{d\left(sin\theta\frac{d\Theta}{d\theta}\right)}{d\theta}+sin^2\theta\; l(l+1)=m_l^2$$

and

$$\frac{-1}{\Phi}\frac{d^2\Phi}{d\varphi^2}=m_l^2$$

The solution to the simple differential equation in φ is:

$$\Phi(\varphi)=e^{im_l\varphi}$$

And as $\Phi(\varphi+2\pi)=\Phi(\varphi)$ (this is a periodic boundary condition resulting from the definition of φ, see figure 1) m_l is an integer. Therefore $m_l = \cdots-3,-2,-1,0,1,2,3\ldots$

As for the equation in θ, it rearranges into:

$$\sin\theta\frac{d(\sin\theta\frac{d\Theta}{d\theta})}{d\Theta}+\Theta\{sin^2\theta\; l(l+1)-m_l^2\}=0$$

This is a form of the Legendre differential Equation.

The solutions to this have been worked out by our mathematician colleagues, they are of the form:

$$\Theta(\theta)=A\,P_l^{m_l}(\cos\theta)$$

where $P_l^{m_l}(x)$ is the associated Legendre function, given by:

$$P_l^{m_l}(x)\equiv(1-x^2)^{\frac{|m_l|}{2}}\left(\frac{\partial}{\partial x}\right)^{|m_l|}P_l(x)$$

and where $P_l(x)$ is the Legendre Polynomial

$$P_l(x)=\frac{1}{2^l l!}(\frac{d}{dx})^l(x^2-1)^l$$

All of this is mathematically complicated and for the time being does not offer any obvious physical insight. There are two important points to consider, however:

a) The solutions involve a polynomial of order l, therefore l is an integer: $l = 0, 1, 2 \ldots$

b) Taking the $|m_l|$ th derivative of a polynomial of order l is non zero only if $|m_l| \leq l$, therefore the value of (the modulus of) m_l cannot exceed that of l. More simply: $m_l = -l \ldots -1, 0, 1 \ldots l$

Of course, the latter implies that there are $(2l+1)$ values of m_l for each value of l.

We can now write normalised angular wavefunctions, called Spherical Harmonics, in their most general form:

$$Y_l^{m_l}(\theta, \varphi) = \epsilon \underbrace{\sqrt{\frac{(2l+1)(l-|m_l|)!}{4\pi(l+|m_l|)!}}}_{\text{Normalisation constant}} \underbrace{e^{i\varphi m_l}}_{\Phi(\varphi)} \underbrace{P_l^{m_l}(\cos\theta)}_{\Theta(\theta)}$$

where $\epsilon = (-1)^{m_l}$ for $m_l \geq 0, = 1$ otherwise.

We note that an individual spherical harmonic depends both on l and m_l, and given that there are $(2l+1)$ values of m_l for every value of l, the number of harmonics grows quickly with l. The general expression given above is quite complicated but it can be dissected into familiar parts such as a normalisation constant, a complex exponential $\Phi(\varphi)$ which includes the value of m_l and a polynomial in either $\sin\theta$ or $\cos\theta$ of order l.

To illustrate this, the first few (up to $l = 2$) spherical harmonics are:

$$Y_0^0 = \sqrt{\frac{1}{4\pi}}$$

$$Y_1^0 = \sqrt{\frac{3}{4\pi}} cos\theta \qquad Y_1^{\pm1} = \mp\sqrt{\frac{3}{8\pi}} sin\theta\, e^{\pm i\varphi}$$

$$Y_2^0 = \sqrt{\frac{5}{16\pi}}(3cos^2\theta - 1) \qquad Y_2^{\pm1} = \mp\sqrt{\frac{15}{8\pi}} sin\theta\, cos\theta e^{\pm i\varphi} \qquad Y_2^{\pm2} = \sqrt{\frac{15}{8\pi}} sin^2\theta\, e^{\pm 2i\varphi}$$

It is well worth noting that spherical harmonics have many applications that range beyond quantum mechanics.

Having dealt with the angular portion of the wavefunction, which does not depend on the specific potential used, other than it being radial, it is now time to consider the radial part of the wavefunction. After the initial separation of variables we obtained:

$$\frac{d(r^2 \frac{dR}{dr})}{dr} - \frac{2mr^2}{\hbar^2}(V - E)R = l(l+1)R$$

Using the substitution $U(r) = rR(r)$ we can rewrite the radial equation as:

$$\frac{-\hbar^2}{2m}\frac{d^2U(r)}{d^2r^2} + U(r)\left(V(r) + \frac{\hbar^2}{2mr^2}l(l+1)\right) = EU(r)$$

This looks just like the time-independent Schrödinger equation, although it is written in terms of *U(r)* and includes an extra term, $\frac{\hbar^2}{2mr^2}l(l+1)$ (which we will later identify as a rotational kinetic energy term).

At this point we can actually substitute the electrostatic potential

$$V(r) = \frac{-e^2}{4\pi\varepsilon_o}.\frac{1}{r}$$

to get

$$\frac{-\hbar^2}{2m}\frac{d^2U}{d^2r^2} + \left[\frac{-e^2}{4\pi\varepsilon_0}.\frac{1}{r} + \frac{-\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]U = EU$$

In order to proceed with the solution we need to define: $k = \sqrt{\frac{-2mE}{\hbar^2}}$

And note that we are interested in the bound state solutions where k is real, as $E \leq 0$. We thus obtain

$$\frac{1}{k^2}\frac{d^2U}{dr^2} = \left[1 - \frac{me^2}{4\pi\varepsilon_o\hbar^2k}.\frac{1}{(kr)} + \frac{l(l+1)}{(kr)^2}\right]U$$

Let us now define the terms $\rho = kr$ and $\rho_0 = \frac{me^2}{4\pi\varepsilon_0\hbar^2k}$ and obtain the somewhat simpler expression:

$$\frac{d^2U}{d\rho^2} = [1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2}]U$$

The solutions to the above are not obvious, but we can consider its asymptotic behaviour.

By taking limit to $\rho \to \infty$ we get: $U(\rho) \sim Ae^{-\rho}$

And by taking Limit to $\rho \to 0$ we get: $U(\rho) \sim C\rho^{l+1}$

In order to account for the whole range of ρ we make use of a third (as yet unspecified) function of ρ, namely $v(\rho)$, and write the overall solution as

$$u(\rho) = \rho^{l+1}e^{-\rho}v(\rho)$$

When we substitute this into $\frac{d^2U}{d\rho^2} = [1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2}]U$ we obtain

$$(\rho_0 - 2l - 2)v + 2(l + 1 - \rho)\frac{dv}{d\rho} + \rho\frac{d^2v}{d\rho^2} = 0$$

As we do not know the exact mathematical form of $v(\rho)$ we have to proceed by writing it in the general form of a power series in ρ:

$$v(\rho) = \sum_{j=0}^{\infty} a_j \rho^j$$

This then implies the recursion relation:

$$a_{j+1} = \left(\frac{2(j+l+1) - \rho_0}{(j+1)(j+2l+2)}\right) a_j$$

The recursion relation can yield all the coefficients of the powers of ρ. This allows us in principle to evaluate the whole series but has an important implication. In order for the series to be finite (and not therefore tend to infinity!) the series must terminate. This will happen when the numerator of the recursion relation is 0 at some maximum power of j, namely j_{max}. So:

$$2(j_{max} + l + 1) - \rho_0 = 0$$

We can finally define n, the principal quantum number as: $n = j_{max} + l + 1$ and we note that this is just an integer (n = 1, 2, 3, 4…). This definition has two important consequences:

a) Since $j_{max} \geq 0$ then the integer values of *l* are constrained by *n* and the relation: $l \leq n - 1$

b) Since $2n = \rho_0$ with $\rho_0 = \frac{me^2}{4\pi\varepsilon_o \hbar^2 k}$ and $k = \sqrt{\frac{-2mE}{\hbar^2}}$, then the value of n determines the energy E of the electron.

The latter point allows us to obtain the Bohr Equation for the allowed electronic energy levels of the hydrogen atom:

$$E_n = -\left\{\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_o}\right)^2\right\}\frac{1}{n^2} = -13.6\frac{1}{n^2}eV = \frac{E_1}{n^2}$$

With $n = 1, 2, 3 \ldots$ These energies are negative as they correspond to bound states consistent with a vacuum level that is defined to be zero. We can also define the Bohr radius:

$$a = \frac{4\pi\varepsilon_o\hbar^2}{me^2} = 0.529\text{x}10^{-10}\text{m}$$

This radius can be used, amongst other things, to simplify the form of the radial solutions. We also note that it implies an *atomic size* of an Angstrom, using only fundamental constants.

We have already established that the full electronic wavefunction $\psi_{n,l,m_l}(r,\theta,\varphi)$ is simply the product of a radial part, which depends on *n* and *l* only, and a spherical harmonic which depends on *l* and m_l only i.e.

$$\psi_{n,l,m_l}(r,\theta,\varphi) = R_{n,l}(\mathrm{r})Y_l^{ml}(\theta,\varphi)$$

where

$$R_{n,l}(\mathrm{r}) = \frac{1}{r}\rho^{l+1}e^{-\rho}v(\rho) \qquad \text{and} \qquad Y_l^{ml}(\theta,\varphi) = C\, e^{im_l\varphi}P_l^{m_l}(\cos\theta)$$

The three quantum numbers and their constraints are:

Principal Quantum Number, $n = 1, 2, 3, \dots$

Orbital Angular Momentum Quantum Number, $l = 0, 1, 2, \dots (n-1)$

Orbital Magnetic Quantum Number, $m_l = -l, \dots -1, 0, 1, \dots + l$

At this point it is worth noting that we can write $v(\rho)$ as:

$$v(\rho) = L_{n-l-1}^{2l+1}(2\rho)$$

where $L_{q-p}^{p}(x)$ is the Associated Laguerre Polynomial given by $L_{q-p}^{p}(x) = (-1)^p (\frac{d}{dx})^q \, (e^{-x}x^q)$

Once again the mathematical complexity of the radial wavefunction can appear daunting so it is worth looking at the first few radial wavefunctions of the Hydrogen atom. The normalised radial wavefunctions can been written in terms of the Bohr radius, a, as:

$R_{1,0} = 2a^{\frac{-3}{2}}e^{-\frac{r}{a}}$

$R_{2,0} = \frac{1}{\sqrt{2}}a^{\frac{-3}{2}}\left(1 - \frac{r}{2a}\right)e^{-\frac{r}{2a}}$, $R_{2,1} = \frac{1}{\sqrt{24}}a^{\frac{-3}{2}}\frac{r}{a}e^{-\frac{r}{2a}}$

$R_{3,0} = \frac{2}{\sqrt{27}}a^{\frac{-3}{2}}\left(1 - \frac{2r}{3a} + \frac{2}{27}\left(\frac{r}{a}\right)^2\right)e^{-\frac{r}{3a}}$, $R_{3,1} = \frac{8}{27\sqrt{6}}a^{\frac{-3}{2}}\left(1 - \frac{r}{6a}\right)\left(\frac{r}{a}\right)e^{-\frac{r}{3a}}$, $R_{3,2} = \frac{4}{81\sqrt{30}}a^{\frac{-3}{2}}\left(\frac{r}{a}\right)^2 e^{-\frac{r}{3a}}$

We can see that they follow a general form where $R_{n,l} \propto e^{\frac{-r}{na}}$ multiplied by a polynomial in *r* with the highest power of $\left(\frac{r}{a}\right)$ being *n* - 1.

We note that we have written the full Hydrogen wavefunction as the product of a *normalised* radial and a *normalised* spherical harmonic function i.e. $\psi_{n,l,m_l}(r,\theta,\varphi) = R_{n,l}(\mathrm{r})Y_l^{ml}(\theta,\varphi)$. That is, the radial and spherical functions have each been normalised separately. This has been achieved by considering the normalisation condition for a single electron in three dimensions:

$$1 = \int \Psi^*\Psi dV = \int |\psi|^2 dV$$

Using $\psi(r,\theta,\varphi) = R(r)Y(\theta,\varphi)$ and a volume element $dV = r^2 sin\theta \; dr \; d\theta \; d\varphi$ in spherical polar coordinates to obtain

$$1 = \int_0^\infty r^2|R|^2 \, dr \int_{\theta=0}^{\theta=\pi} \int_{\varphi=0}^{\varphi=2\pi} sin\theta|Y|^2 \; d\varphi \; d\theta$$

This, of course, implies that *radially* the probability of detecting the electron in the element between *r* and *r* + *dr* is given by:

$$r^2|R(r)|^2 \, dr$$

The time has come to look at angular momentum in Quantum Mechanics and the physical significance of l and m_l in detail. Classically the angular momentum of a particle about the origin is defined, using its position and linear momentum, by $\vec{L} = \vec{r} \times \vec{p}$. The angular momentum is a vector and we can write it in terms of its components, L_x, L_y, L_z. This is also true of the position whose components are simply x, y, z and the linear momentum whose components are $p_x,\ p_y,\ p_z$.

Using the properties of the cross product, each component can be written as

$$L_z = xp_y - yp_x \ \ , L_y = zp_x - xp_z \text{ and } L_x = yp_z - zp_y$$

We remind ourselves that quantum mechanically the momentum operator can be written as:

$$\widehat{p_y} = -i\hbar \frac{\partial}{\partial y} \quad \text{or} \quad \widehat{p_x} = -i\hbar \frac{\partial}{\partial x} \quad \text{or} \quad \widehat{p_z} = -i\hbar \frac{\partial}{\partial z}$$

So the operator corresponding to the z-component of the angular momentum is:

$$\widehat{L_z} = -i\hbar(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}) .$$

We also apply this approach when considering the magnitude (or modulus squared) of the angular momentum itself and write: $|\widehat{L}|^2 = \widehat{L_x}^2 + \widehat{L_y}^2 + \widehat{L_z}^2$

All of the above has been applied using Cartesian coordinates and once again we require the differential operators in spherical polar form. The two main operators in spherical coordinates become:

$$\widehat{L_z} = -i\hbar\frac{\partial}{\partial\varphi} \quad \text{and} \quad \widehat{L^2} = -\hbar^2[\frac{1}{\sin\theta}\frac{\partial\left(\sin\theta\frac{\partial}{\partial\theta}\right)}{\partial\theta} + \frac{1}{sin^2\theta}\frac{\partial^2}{\partial\varphi^2}]$$

We can then apply these operators to the wavefunction:

$$\psi(r,\theta,\varphi) = R(\mathrm{r})\mathrm{Y}(\theta,\varphi) = R(r)\Theta(\theta)e^{im_l\varphi}$$

The first equation we obtain is $\widehat{L_z}\psi = -i\hbar\frac{\partial\left(R\Theta e^{im_l\varphi}\right)}{\partial\varphi}$, yielding the elegant eigenvalue equation:

$$\widehat{L_z}\psi = \hbar m_l\psi$$

The second equation we obtain is $\widehat{L^2}\psi = -\hbar\left[\frac{1}{sin\,\theta}\frac{\partial(sin\,\theta\frac{\partial}{\partial\theta})}{\partial\theta} + \frac{1}{sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]R\Theta e^{im_l\varphi}$, which (after some manipulation) yields a second eigenvalue equation:

$$\widehat{L^2}\psi = \hbar^2\, l(l+1)\psi$$

These are extremely important results:

First they tell us that angular momentum itself is quantised, and that the natural unit for angular momentum is $\hbar$ itself. Second, they imply that the magnitude of the orbital angular momentum is simply determined by l and that it is given by: $|\vec{L}| = \hbar\sqrt{l(l+1)}$.

The third result is that the orbital angular momentum has a distinct number of projections along a given axis, z. These projections, or components, are given by $L_z = \hbar m_l$, so they are determined by the orbital magnetic quantum number m_l and there are $2l + 1$ such values allowed.

They also tell us that our wavefunctions ψ_{n,l,m_l} are simultaneous eigenfunctions of all three quantum numbers as summarised below.

Quantity	Energy	$\lvert\vec{L}\rvert$	L_z
Quantum Number	n	l	m_l
Value	$13.6\frac{1}{n^2}eV$	$\hbar\sqrt{l(l+1)}$	$\hbar m_l$

Visualising these results is greatly aided by considering the angular momentum vector as a vector precessing about the z-axis as shown in figure 2 (drawn for an arbitrary value of l).

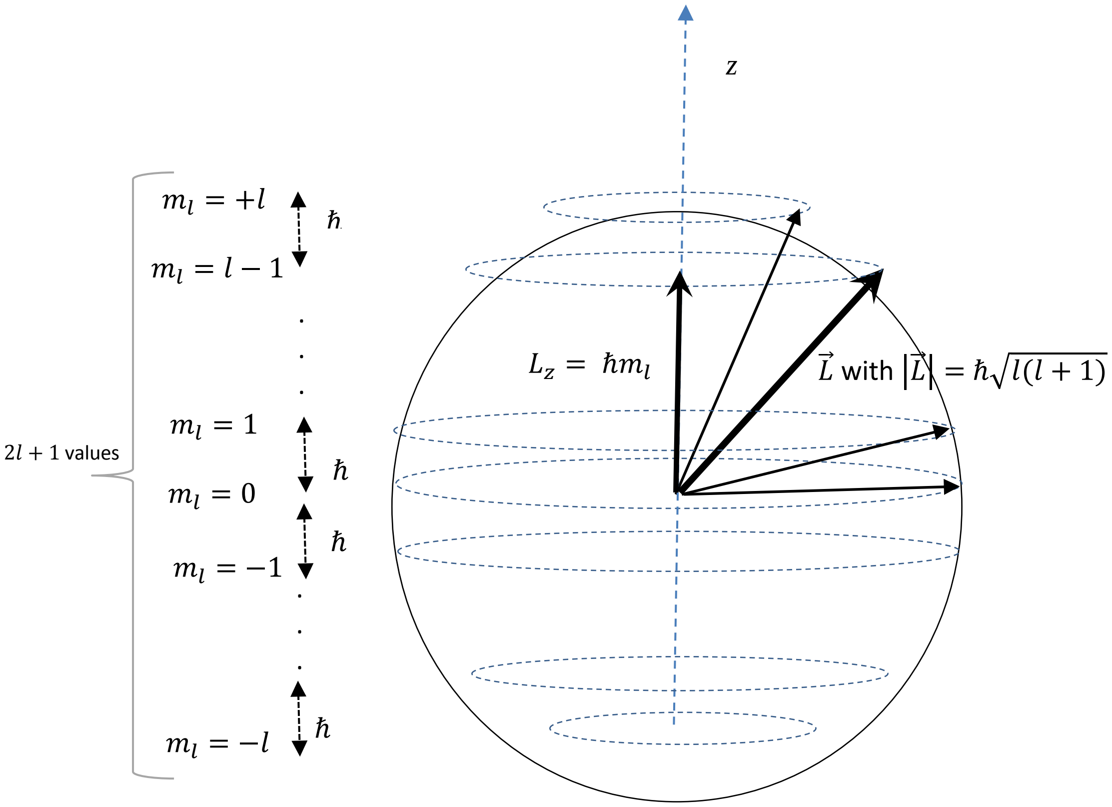


Figure 2: *A vector diagram representing the angular momentum and its possible projections. We can imagine these as confined within a sphere of radius* $\hbar\sqrt{l(l+1)}$.

In order to fully consider all the possible electronic states for the Hydrogen atom we have to take into account *spin* angular momentum in addition to *orbital* angular momentum. As electrons have spin = $\frac{1}{2}$ (i.e. they have by their very nature s = ½) there are two possible projections of this spin angular momentum about the z-axis, $m_s = \pm\frac{1}{2}$. These are often referred to as spin-up and spin-down and denoted using the short hand $(\uparrow, \downarrow)$.

The full electronic wavefunction will depend on all four quantum numbers and thus becomes:

$$\psi_{n,l,m_l,m_s}(r, \theta, \varphi)$$

With the values of the quantum numbers given by:

Principal Quantum Number, $n = 1, 2, 3, \ldots$

Orbital Angular Momentum Quantum Number, $l = 0, 1, 2, \ldots (n-1)$

Orbital Magnetic Quantum Number, $m_l = -l, \ldots -1, 0, 1, \ldots +l$ ($2l + 1$ values)

Spin Magnetic quantum number, $m_s = +\frac{1}{2}, -\frac{1}{2}$ ($2s + 1 = 2$ values for $s = \frac{1}{2}$)

In the absence of any external magnetic fields, the energy of the electron in the Hydrogen atom is only dictated by the principal quantum number. The resulting energy levels have increasing degeneracy with increasing n. An energy diagram for the Hydrogen atom is shown schematically in figure 3 and illustrates that the energy level degeneracy is given by $2n^2$.

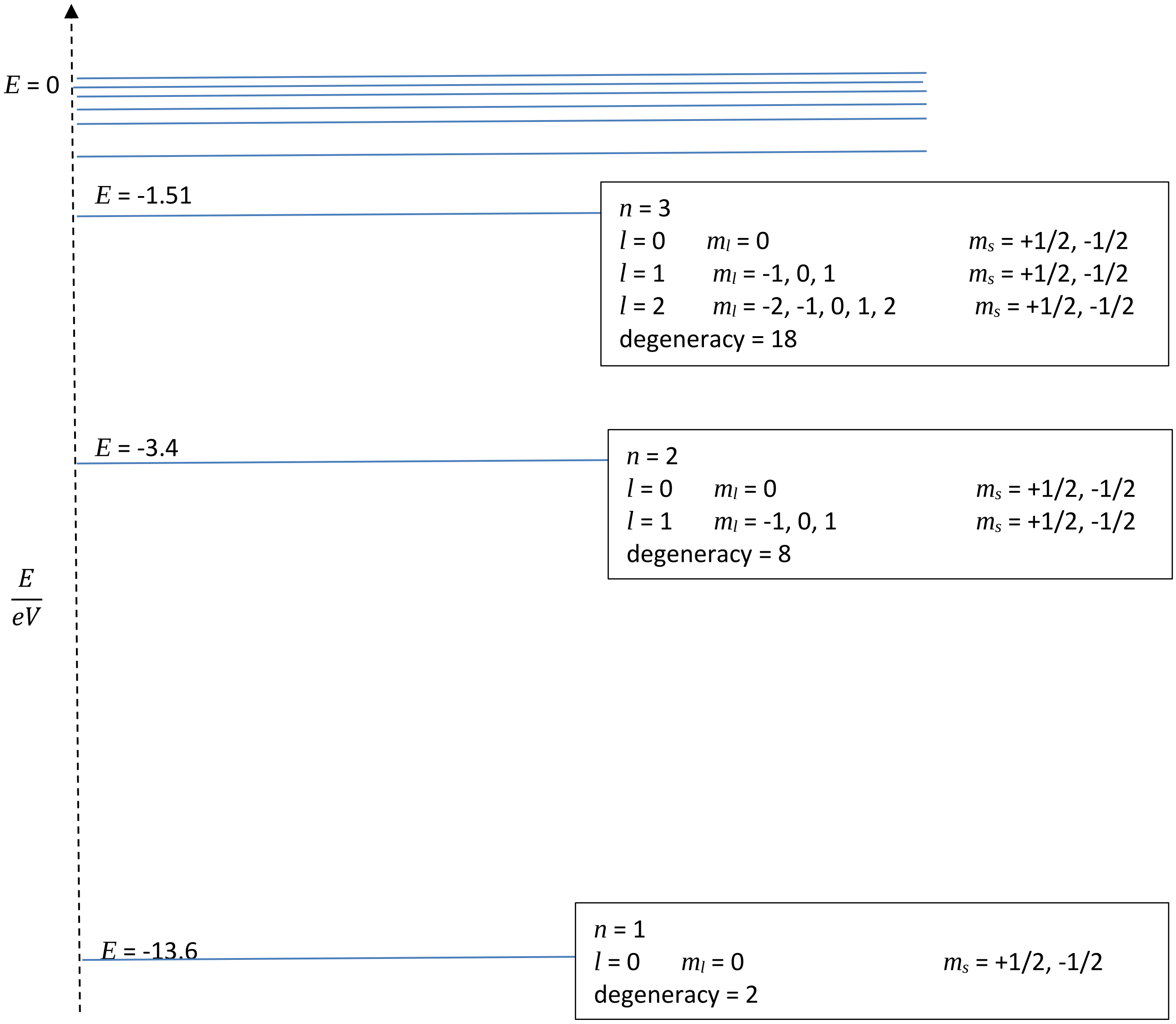


Figure 3: *Schematic energy diagram for the Hydrogen atom.*