

## Lectures 19&20: The Spherical Harmonics

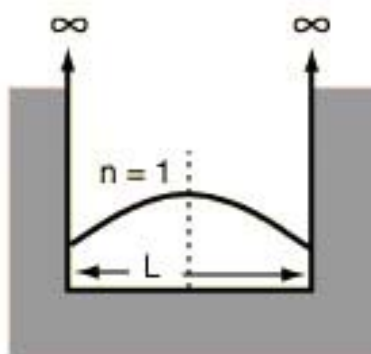
References: Course Pack p.83-86, 125-128.

In the last lecture, we stated that for spherical polar coordinates,

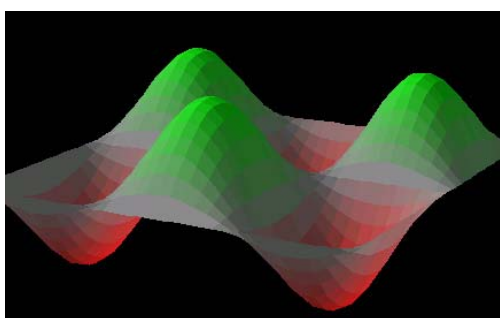
$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}.$$

We also stated that solutions which are spherically symmetric are only a function of radius. Now we move to the more general case of solutions which depend on  $r$ ,  $\theta$  and  $\phi$ . In this case we need to consider the full form of  $\nabla^2$ , as given above.

Spherical harmonics are very tricky to visualise in 3D. Whilst everyone can imagine both the ground state of a particle in an infinite quantum well and the 2D representation of 2 harmonics of a wave distribution in  $x$  and  $y$  interacting on a plate (as shown below) it is another matter entirely to visualise the spherical harmonics that you would expect in a 3D spherical potential well !!!



$x = 0$  at left wall of box.



To help visualisation we will base our discussion around the hydrogen atom and its various energy states.

Bohr and Schrodinger both predicted that the energy levels of the H atom were:  $E_n = -\frac{13.6\text{eV}}{n^2}$

This means that the energy of an electron in any excited orbital depends purely on the energy level in which it resides. From your knowledge of chemistry, you will know that each energy level can contain more than one electron. These electrons must therefore have the same energy.

An electron probability cloud (EPC) is a schematic representation of the likely position of an electron at any time. The figure below shows the EPCs corresponding to the ground state and some excited states of the hydrogen atom. As you can see for each energy level there are several different electron probability cloud distributions corresponding to the different 3D harmonic solutions at that level.

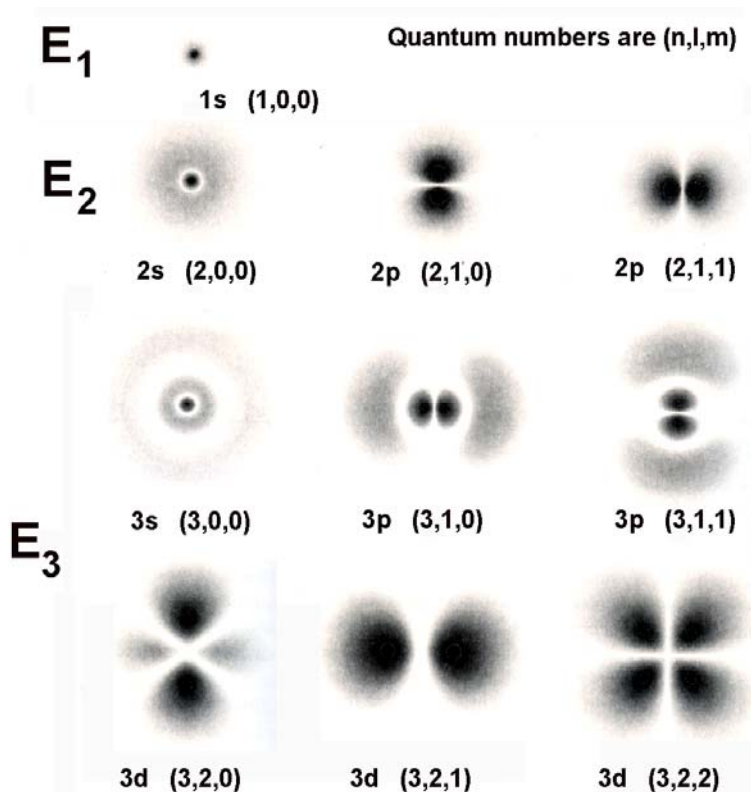
In Quantum Mechanics we would say that there exists more than one quantum state corresponding to each energy level of the H atom. (Actually there are  $2n^2$  different quantum states for the  $n^{\text{th}}$  energy level).

For the 1D case in Quantum Mechanics it was sufficient to define a quantum state fully using just one quantum number, e.g.  $n = 2$  because our well extended only along the  $x$  axis. However in 2D and 3D we have to consider multiple axes within a 3D potential well, and since the probability density functions corresponding to the EPCs are mostly not radially symmetric, we must represent wavefunctions with the same energy but different eigenfunctions, using a unique set of quantum numbers.

Of the 3 quantum numbers used to represent the special geometry of spherical waves in 3D,  $n$  is defined as the principal quantum number (and sets the value of the energy level of the wave). For each wave with quantum number  $n$ , there exist  $(n - 1)$  quantum states of  $l$  from  $l = 0$  to  $l = (n - 1)$  where  $l$  is defined as the orbital quantum number. So for example an electron in the 3<sup>rd</sup> excited state can be in  $(n=3, l=0)$ , or  $(n=3, l=1)$  or  $(n=3, l=2)$  quantum states.

In addition each one of these quantum states has further states represented by another quantum number  $m$  defined as the magnetic quantum number. Whereas  $l$  is a positive integer,  $m$  is a positive or negative integer where  $|m| \leq l$ . This means that for a given  $l$ , there are  $2l+1$  allowed values of  $m$ :  
 $m = 0, \pm 1, \pm 2, \dots, \pm l$ .

(A 4<sup>th</sup> quantum number defines spin - an intrinsic property of the particle - but since this does not influence spatial geometry it will not be detailed here except to say that for every combination of  $n, l, m$  there also exists an additional spin up and spin down configuration. All these combine to make up the total  $2n^2$  different quantum states mentioned earlier.)



Since the most important quantum numbers are  $n$  and  $l$ , we typically refer to them using a combination of the numerical value of  $n$ , and a letter to represent  $l$  as shown in the table below.

Quantum number	Standard terminology for $n$	Standard terminology for $l$
0		s
1	1 (K shell)	p
2	2 (L shell)	d
3	3 (M shell)	f

All combinations of quantum numbers characterising the ground state, 1<sup>st</sup> and 2<sup>nd</sup> excited states are shown below.

State	Principal quantum number $n$	Orbital quantum number	Magnetic quantum number	Spin quantum number	Maximum number of electrons
1s	1	0	0	$+\frac{1}{2}, -\frac{1}{2}$	2
2s	2	0	0	$+\frac{1}{2}, -\frac{1}{2}$	2
2p	2	1	-1, 0, +1	$+\frac{1}{2}, -\frac{1}{2}$	6
3s	3	0	0	$+\frac{1}{2}, -\frac{1}{2}$	2
3p	3	1	-1, 0, +1	$+\frac{1}{2}, -\frac{1}{2}$	6
3d	3	2	-2, -1, 0, 1, 2	$+\frac{1}{2}, -\frac{1}{2}$	10

The electron in the hydrogen atom sees a spherically symmetric potential, so it is logical to use spherical polar coordinates to develop the Schrodinger equation.

In 3D Cartesian coordinates the time independent Schrodinger equation can be written as:

$$-\frac{\hbar^2}{2m} \left[ \frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} \right] + V(x, y, z) \Psi(x, y, z) = E \Psi(x, y, z) \quad \text{i.e.} \quad -\frac{\hbar^2}{2m} \nabla^2 \Psi + V(x, y, z) \Psi(x, y, z) = E \Psi(x, y, z)$$

Since  $\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}$  in spherical polar coordinates,

the time independent Schrodinger equation becomes:  $-\frac{\hbar^2}{2m} \nabla^2 \Phi(r, \theta, \phi) + V(r) \Phi(r, \theta, \phi) = E \Phi(r, \theta, \phi)$

It is well beyond the scope of this course to solve the 3D TISE but it can be shown (eventually) that the solution as usual can be written as:

$$\Psi(r, \theta, \phi) = R(r)P(\theta)F(\phi)$$

in which each function for the three spatial variables gives rise and is therefore associated with the three quantum numbers associated with the spatial geometry of the hydrogen energy levels.

The function  $R(r)$  contains the solution to the radial part of the TISE and the principal quantum number dependency  $n$ . The function  $P(\theta)$  determines the magnitude of the orbital angular momentum and defines the orbital quantum number dependency  $l$ , and the function  $F(\phi)$  contains the magnetic quantum number dependency  $m$ .

The full solution  $\Psi(r, \theta, \phi) = R(r)P(\theta)F(\phi)$ , for the ground state and first few excited states corresponding to each specific combination of quantum numbers is shown below.  $a_0$  is the first Bohr radius corresponding to the ground state of the H atom .....

Quantum numbers for 3D spatial geometry			Normalised solution of the TISE for Hydrogen atom		
$n$	$l$	$m$	$R(r)$	$P(\theta)$	$F(\phi)$
1	0	0	$\frac{2}{a_0^{3/2}} e^{-r/a_0}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2\pi}}$
2	0	0	$\frac{1}{2\sqrt{2}a_0^{3/2}} \left[ 2 - \frac{r}{a_0} \right] e^{-r/2a_0}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2\pi}}$
2	1	0	$\frac{1}{2\sqrt{6}a_0^{3/2}} \left[ \frac{r}{a_0} \right] e^{-r/2a_0}$	$\frac{\sqrt{6}}{2} \cos \theta$	$\frac{1}{\sqrt{2\pi}}$
2	1	$\pm 1$	$\frac{1}{2\sqrt{6}a_0^{3/2}} \left[ \frac{r}{a_0} \right] e^{-r/2a_0}$	$\frac{\sqrt{3}}{2} \sin \theta$	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$
3	0	0	$\frac{2}{81\sqrt{3}a_0^{3/2}} \left[ 27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2} \right] e^{-r/3a_0}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2\pi}}$
3	1	0	$\frac{4}{81\sqrt{6}a_0^{3/2}} \left[ 6 - \frac{r}{a_0} \right] \frac{r}{a_0} e^{-r/3a_0}$	$\frac{\sqrt{6}}{2} \cos \theta$	$\frac{1}{\sqrt{2\pi}}$
3	1	$\pm 1$	$\frac{4}{81\sqrt{6}a_0^{3/2}} \left[ 6 - \frac{r}{a_0} \right] \frac{r}{a_0} e^{-r/3a_0}$	$\frac{\sqrt{3}}{2} \sin \theta$	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$
3	2	0	$\frac{4}{81\sqrt{30}a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{\sqrt{10}}{4} (3\cos^2 \theta - 1)$	$\frac{1}{\sqrt{2\pi}}$

Once we have the solution to the wave equation in 3D spherical polar coordinates we can deduce the probability function.

For example the probability density function in 3D for the ground state (1,0,0) is found as follows.....

$$\text{For the (1,0,0) harmonic mode } \Psi(r, \theta, \phi) = R(r)P(\theta)F(\phi) = \frac{2}{a_0^{3/2}} e^{-r/a_0} \frac{1}{\sqrt{2}} \frac{1}{\sqrt{2\pi}} = \frac{1}{\sqrt{\pi} a_0^{3/2}} e^{-r/a_0}$$

$$\text{So } |\Psi(r, \theta, \phi)|^2 = \left( \frac{1}{\sqrt{\pi} a_0^{3/2}} e^{-r/a_0} \right)^2 = \frac{1}{\pi a_0^3} e^{-2r/a_0}$$

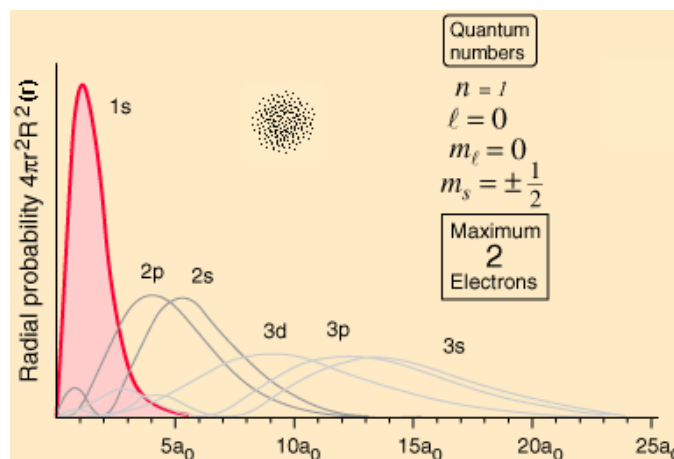
It takes this comparatively simple form because the 1s state is spherically symmetric and therefore no angular terms appear. The radial probability density for the hydrogen ground state is obtained by multiplying the square of the wavefunction by a spherical shell volume element.

$$dP = \frac{1}{\pi a_0^3} e^{-2r/a_0} 4\pi r^2 dr$$

If we integrate over all space between  $0 \leq r \leq \infty$  we can show that the total probability is 1.

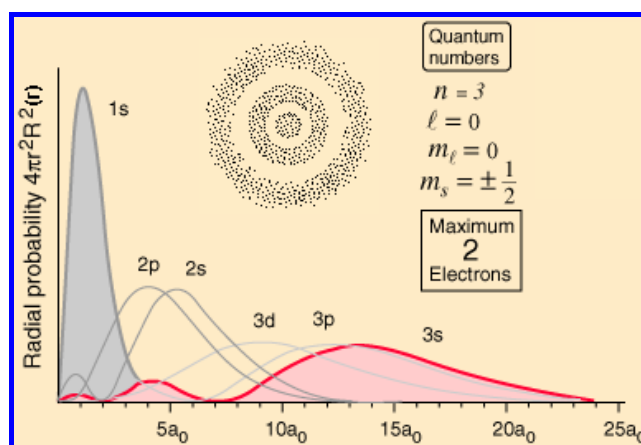
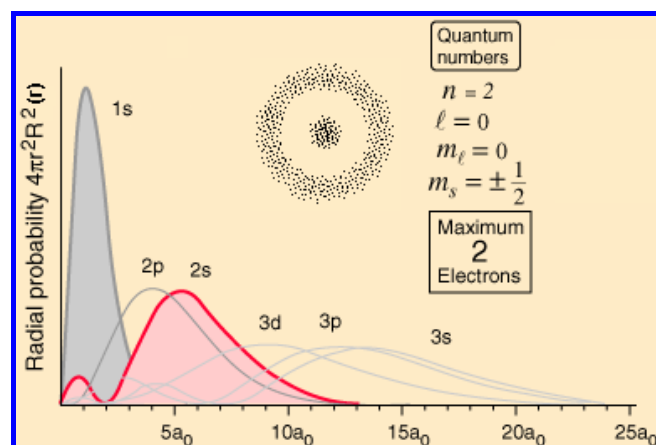
$$P = \int_0^\infty \frac{1}{\pi a_0^3} e^{-2r/a_0} 4\pi r^2 dr = \int_0^\infty \frac{4r^2}{a_0^3} e^{-2r/a_0} dr$$

$$P = \frac{4}{a_0^3} \left[ e^{-2r/a_0} \left( \frac{-a_0 r^2}{2} - \frac{a_0^2 r}{2} - \frac{a_0^3}{4} \right) \right]_0^\infty = 1$$



It would be very interesting to plot the full 3D probability density distributions for each combination of quantum states. Unfortunately, distributions for non spherically symmetric solutions (i.e.  $p$  and  $d$  quantum states) would be a function of  $\theta$  and  $\phi$  as well as of radius  $r$  making them exceedingly difficult to plot.

If instead we were to plot only the probability density functions for spherically symmetric solutions (i.e.  $s$  quantum states) for each quantum state  $n$  we would find the following distributions corresponding to the EPCs shown earlier for hydrogen.

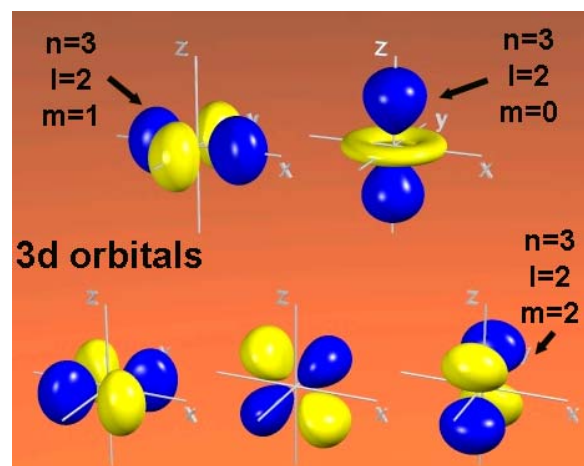


From Hyperphysics website: <http://hyperphysics.phy-astr.gsu.edu/Hbase/hydwf.html#c1>

The **radial** probability density distributions for other quantum states can be found at the above website.

We must remember that these plots are 3 dimensional in so far as they describe the probability that an electron may be found at a specific location within a 3 dimensional spherical potential well.

The 3D representation of the  $3d$  orbital shown as an EPCs for hydrogen earlier would look like.....



This figure shows the various geometric configurations of the 3d orbitals in 3 dimensions.

<http://winter.group.shef.ac.uk/orbitron/AOs/3d/index.html>

## Spherical Harmonics

If, as we have done, we define the solution of a PDE expressed in spherical polar coordinates as  $\Psi(r, \theta, \phi) = R(r)P(\theta)F(\phi)$  then we can say that the solution is comprised of a radially dependent function  $R(r)$  and two angular dependent terms  $P(\theta)F(\phi)$  which can be grouped together to form specific spherical harmonic solutions  $Y_l^m(\theta, \phi)$ . Formally the spherical harmonics  $Y_l^m(\theta, \phi)$  are the angular portion of the solution to Laplace's equation in spherical coordinates derived in the appendix.  $Y_l^m(\theta, \phi)$  are found in the solution of any PDE which contains no explicit angular dependence. The derivation of their properties is beyond the scope of this course. As stated earlier,  $l$  is a positive integer,  $m$  is a positive or negative integer and  $|m| \leq l$ . This means that for a given  $l$ , there are  $2l+1$  allowed values of  $m$ :  $m = 0, \pm 1, \pm 2, \dots, \pm l$ . Hence there are  $2l + 1$  different functions  $Y_l^m(\theta, \phi)$  for each value of  $l$ . The spherical harmonics  $Y_l^m(\theta, \phi)$  are listed in the appendix and can be directly compared with the  $P(\theta)$  and  $F(\phi)$  solutions for the wave function describing the electron orbitals of the hydrogen atom.

Spherical harmonics are useful in an enormous range of applications, not just the solving of PDEs. It means a complicated function of  $\theta$  and  $\phi$  can be parameterised in terms of a set of solutions. The different harmonics can often be related to different physical phenomena or characteristics (e.g. in electrostatics, the potential due to a monopole, dipole, quadrupole, etc.). The shape of the earth (nearly but not exactly spherical), anisotropic potential variation, and the shape of a nucleus are just a few examples of non-spherical functions which it can be helpful to express as a sum over spherical harmonics.

## Summary

1. Similarly to the solution in 1D and 3D Cartesian coordinates, the Laplace equation, wave equation, diffusion equation and Schrödinger equation (for a central potential) can be solved in spherical polar coordinates by separation of the variables.
2. In *all* cases, the solutions are all of the form  $T(t)R_l(r)Y_l^m(\theta, \phi)$ . The functions  $T(t)$  and  $R_l(r)$  depend on the equation being solved, but for *all* the equations the angular dependence is given by the spherical harmonics  $Y_l^m(\theta, \phi)$ .
3. The functional form of the spherical harmonics can be looked up in a table when required.
4.  $l$  is a positive integer,  $m$  may be positive or negative, and  $|m| \leq l$  so there are  $2l+1$  different  $Y_l^m(\theta, \phi)$  for each value of  $l$ .

This mathematics underlies not only the whole of atomic and nuclear physics but also many other applications including electrostatics, electromagnetic radiation, tides, solar oscillations, and many other problems. Next semester in atomic physics you will cover in more detail the radial spherical polar solutions of the Schrödinger equation for the hydrogen atom.

## Appendix

To demonstrate a solution of a PDE in 3D using spherical polar coordinates we will consider the Laplace equation, although the procedure is the same for other more complicated PDEs.

### The Laplace Equation, $\nabla^2 V = 0$ .

As stated in lecture 18, the Laplace equation in spherical polar coordinates is written:

$$\nabla^2 V(r, \theta, \phi) = 0 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial V(r, \theta, \phi)}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial V(r, \theta, \phi)}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 V(r, \theta, \phi)}{\partial \phi^2}.$$

Let us look for solutions of the form  $V(r, \theta, \phi) = R(r) P(\theta) F(\phi)$ ,

Substituting this into the PDE gives:

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d[R(r) P(\theta), F(\phi)]}{dr} \right) + \frac{1}{r^2 \sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d[R(r) P(\theta), F(\phi)]}{d\theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{d^2 [R(r) P(\theta), F(\phi)]}{d\phi^2} = 0$$

then multiplying both sides by  $\frac{1}{[R(r)P(\theta)F(\phi)]}$  in order to separate variables gives:

$$\frac{1}{R(r)} \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR(r)}{dr} \right) + \frac{1}{P(\theta)} \frac{1}{r^2 \sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{dP(\theta)}{d\theta} \right) + \frac{1}{F(\phi)} \frac{1}{r^2 \sin^2 \theta} \frac{d^2 F(\phi)}{d\phi^2} = 0.$$

Multiplying both sides by  $r^2 \sin^2 \theta$  gives:

$$\sin^2 \theta \frac{1}{R(r)} \frac{d}{dr} \left( r^2 \frac{dR(r)}{dr} \right) + \sin \theta \frac{1}{P(\theta)} \frac{d}{d\theta} \left( \sin \theta \frac{dP(\theta)}{d\theta} \right) + \frac{1}{F(\phi)} \frac{d^2 F(\phi)}{d\phi^2} = 0.$$

The first term on the left involves both  $r$  and  $\theta$  so we have not yet fully separated the variables. However  $\phi$  is involved only in the last term on the LHS. So we can say that for the equation to be true for all  $r, \theta, \phi$ , the last term must equal a constant. But should it be positive or negative?

The potential must be **single valued** meaning that at a given point in space it must have just one value. Note that in spherical polar coordinates, the points  $(r, \theta, \phi)$  and  $(r, \theta, \phi + 2\pi)$  are the same point and so we must also have  $F(\phi) = F(\phi + 2\pi)$ . This means we need harmonic solutions, and thus a negative constant.

We choose  $\frac{1}{F(\phi)} \frac{d^2 F(\phi)}{d\phi^2} = -m^2$  where  $m$  is an integer, giving  $F(\phi) \sim \begin{cases} \sin m\phi \\ \cos m\phi \end{cases}$  or  $\begin{cases} e^{im\phi} \\ e^{-im\phi} \end{cases}$ .

Usually the form  $F(\phi) = e^{im\phi}$  is used.

And we need periodicity of  $2\pi$ , i.e. need  $\sin(m\phi) = \sin(m\phi + m2\pi)$ , etc. – which is true if and only if  $m$  is integer.

Replacing the  $\phi$  term with  $-m^2$ , the equation above becomes

$$\sin^2 \theta \frac{1}{R(r)} \frac{d}{dr} \left( r^2 \frac{dR(r)}{dr} \right) + \sin \theta \frac{1}{P(\theta)} \frac{d}{d\theta} \left( \sin \theta \frac{dP(\theta)}{d\theta} \right) - m^2 = 0.$$

Dividing both sides by  $\sin^2 \theta$  gives:

$$\frac{1}{R(r)} \frac{d}{dr} \left( r^2 \frac{dR(r)}{dr} \right) + \frac{1}{P(\theta)} \frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{dP(\theta)}{d\theta} \right) - \frac{m^2}{\sin^2 \theta} = 0.$$

Now the first term involves only  $r$  and the second two terms only involve  $\theta$ . So to be true for all  $r$  and  $\theta$ , the first term must equal a constant. If we call the constant  $B$  then we get the following ODES:

$$\frac{1}{R(r)} \frac{d}{dr} \left( r^2 \frac{dR(r)}{dr} \right) = B \quad \text{giving} \quad \frac{d}{dr} \left( r^2 \frac{dR(r)}{dr} \right) = BR(r)$$

And also

$$\frac{1}{P(\theta)} \frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{dP(\theta)}{d\theta} \right) - \frac{m^2}{\sin^2 \theta} = B \quad \text{giving} \quad \frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{dP(\theta)}{d\theta} \right) - \frac{m^2}{\sin^2 \theta} P(\theta) - BP(\theta) = 0$$

We are not going to solve the equation in  $\theta$ ! It is an equation which has been studied by mathematicians and we are simply going to state its solutions!

The solutions are found to diverge unless  $B = -l(l+1)$  where  $l$  is a positive integer and  $l \geq m$ .

Taking  $B = -l(l+1)$ , the solutions  $P(\theta)$  are real functions known as the *associated Legendre functions*, normally denoted by  $P_l^m(\cos \theta)$ . Note that the functions depend on both  $l$  and  $m$ .

We have  $P(\theta) = P_l^m(\cos \theta)$  and  $F(\phi) \sim e^{im\phi}$ . So we can write  $P(\theta)F(\phi) = Y_l^m(\theta, \phi) = c_{l,m} P_l^m(\cos \theta) e^{im\phi}$ .

The functions  $Y_l^m(\theta, \phi)$  are known as the **spherical harmonics**.

The coefficients are just normalization constants.

Then the solutions to our equation are  $V(r) = R(r) Y_l^m(\theta, \phi)$ .

A table of the first few spherical harmonics  $Y_l^m(\theta, \phi)$

$l$	$m$	$Y_l^m(\theta, \phi)$	Atomic orbital
0	0	$Y_0^0(\theta, \phi) = \frac{1}{\sqrt{4\pi}}$	s
1	0	$Y_1^0(\theta, \phi) = \sqrt{\frac{3}{4\pi}} \cos \theta$	p
	1	$Y_1^1(\theta, \phi) = -\sqrt{\frac{3}{8\pi}} \sin \theta e^{i\phi}$	
	-1	$Y_1^{-1}(\theta, \phi) = \sqrt{\frac{3}{8\pi}} \sin \theta e^{-i\phi}$	
2	0	$Y_2^0(\theta, \phi) = \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1)$	d
	$\pm 1$	$Y_2^{\pm 1}(\theta, \phi) = \mp \sqrt{\frac{5}{24\pi}} 3 \cos \theta \sin \theta e^{\pm i\phi}$	
	$\pm 2$	$Y_2^{\pm 2}(\theta, \phi) = \mp \sqrt{\frac{5}{96\pi}} 3 \sin^2 \theta e^{\pm 2i\phi}$	
3	0	$Y_3^0(\theta, \phi) = \sqrt{\frac{7}{16\pi}} (5 \cos^3 \theta - 3 \cos \theta)$	f
	$\pm 1$	$Y_3^{\pm 1}(\theta, \phi) = \mp \sqrt{\frac{21}{64\pi}} \sin \theta (5 \cos^2 \theta - 1) e^{\pm i\phi}$	
	$\pm 2$	$Y_3^{\pm 2}(\theta, \phi) = \mp \sqrt{\frac{105}{32\pi}} \sin^2 \theta \cos \theta e^{\pm 2i\phi}$	
	$\pm 3$	$Y_3^{\pm 3}(\theta, \phi) = \mp \sqrt{\frac{35}{64\pi}} \sin^3 \theta e^{\pm 3i\phi}$	