

## Worksheet 3 — Solutions to Schrödinger's Equation

### Introduction

In the last worksheet we looked at classical vibrations and waves. This time we will be concentrating on waves in Quantum Physics. In particular we will be looking at the Wave Mechanical formulation of quantum theory, which is governed by Schrödinger's Equation. First we will need some theory and then an improved numerical approximation for differential equations.

### Schrödinger's Wave Equation

In Wave Mechanics, the state of a quantum system is described by its wave-function, *e.g.*  $\psi(x)$  in one dimension. The interpretation of this wave-function is that the probability density of a particle to be at a position  $x$  is given by  $|\psi(x)|^2$ . The shape of the wave-function is governed by the differential equation known as Schrödinger's Equation. For standing states in one dimension it looks like:

$$\frac{d^2\psi(x)}{dx^2} = \frac{2m}{\hbar^2} [V(x) - E] \psi(x) \quad (1)$$

where  $E$  is the energy of the system,  $m$  is the mass of the particle and  $V(x)$  is the form of the potential that the particle is subjected to.

For the purposes of this week's examples, we will not be worrying about the absolute energies or sizes of the solutions, just the functional forms. For this purpose, it is adequate to set constants to appropriate values in order to simplify the equation. So we can re-write equation 1 as:

$$\frac{d^2\psi(x)}{dx^2} = F(x)\psi(x) \quad (2)$$

$$F(x) = V(x) - E \quad (3)$$

During these exercises, we will be changing the shape of the potential  $V(x)$ , so you should define  $F(x)$  as a function appropriate to the exercise.

## A better numerical solution for differential equations

Last week we introduced you to the simplest method of approximation for differential equations. In terms of equation 2, this method would be:

$$\psi(x + \delta x) = \psi(x) + \delta x \frac{d\psi(x)}{dx} \quad (4)$$

$$\frac{d\psi(x + \delta x)}{dx} = \frac{d\psi(x)}{dx} + \delta x \frac{d^2\psi(x)}{dx^2} = \frac{d\psi(x)}{dx} + \delta x F(x)\psi(x) \quad (5)$$

However, this week, we will use the next order of approximation. This will facilitate finding stable solutions, and will reduce the problems seen in last week's exercise when successive approximations went out of control.

Instead of equations 4 and 5 above, we use:

$$\psi(x + \delta x) = \psi(x) + \delta x \frac{d\psi(x + \delta x/2)}{dx} \quad (6)$$

$$= \psi(x) + \delta x \frac{d\psi(x)}{dx} + \frac{1}{2}(\delta x)^2 F(x)\psi(x) \quad (7)$$

and similarly:

$$\frac{d\psi(x + \delta x)}{dx} = \frac{d\psi(x)}{dx} + \delta x \frac{d^2\psi(x + \delta x/2)}{dx^2} \quad (8)$$

$$= \frac{d\psi(x)}{dx} + \delta x F(x + \delta x/2) \left[ \psi(x) + \frac{1}{2}\delta x \frac{d\psi(x)}{dx} \right] \quad (9)$$

There is just one difference — instead of evaluating the slopes at  $x$ , we evaluate them at  $x + \delta x/2$ , which is better, being halfway between  $x$  and  $\delta x$ . This is illustrated in Figure 1, and comparison with last weeks diagram should convince you that this is a better method.

Although this may look complex, to implement this in Mathcad is straight forward. It is essentially the same technique as last week, only with a few more terms. Note that it is called the second order approximation since we now have all the  $(\delta x)^2$  terms as well as the  $\delta x$  terms.

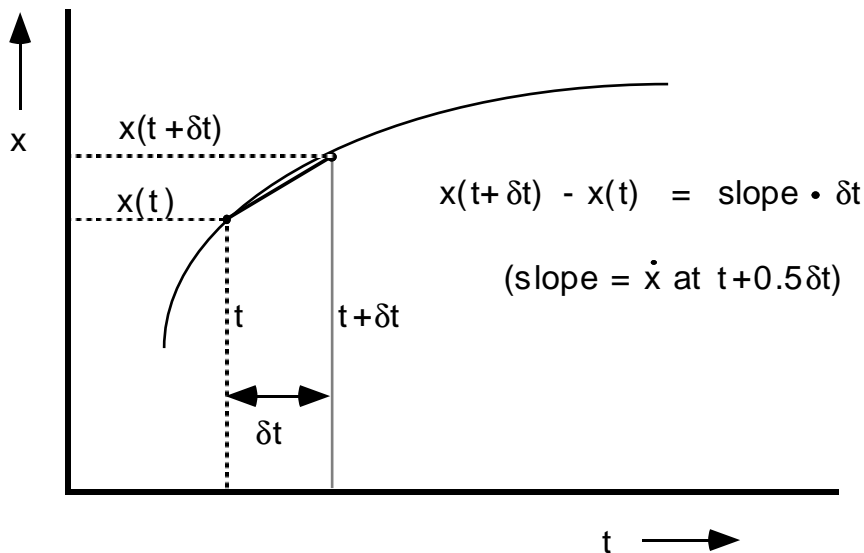


Figure 1: Second order approximation to solve a differential equation.

Week 4, Session 1

# 1 The Step Potential

## 1.1 Individual Standing Waves by Numerical Solution

As a first exercise, we shall try to calculate a solution to the problem of a particle wave hitting a potential barrier which is larger than the energy of the particle. Start with a potential that looks like:

$$\begin{aligned}
 V(x) &= 10 && \text{for } x > 0 \\
 &= 0 && \text{for } x \leq 0
 \end{aligned}
 \tag{10}$$

Using the numerical approximations of equations 8 and 9, write a Mathcad worksheet to plot the values of  $\psi(x)$  for the range  $-10 \leq x \leq 1$ . You will have to decide on suitable step sizes in order to get a good approximation without wasting too much time in calculation. To start with, use an energy of  $E = 1$ , and the initial values:

$$\psi(-10) = 5, \quad \frac{d\psi(-10)}{dx} = 0$$

You should see that the wave-function has the familiar sinusoidal shape until it reaches the potential barrier. When the wave-function hits the potential barrier, it diverges badly, and this solution is therefore non-physical. This is illustrated in

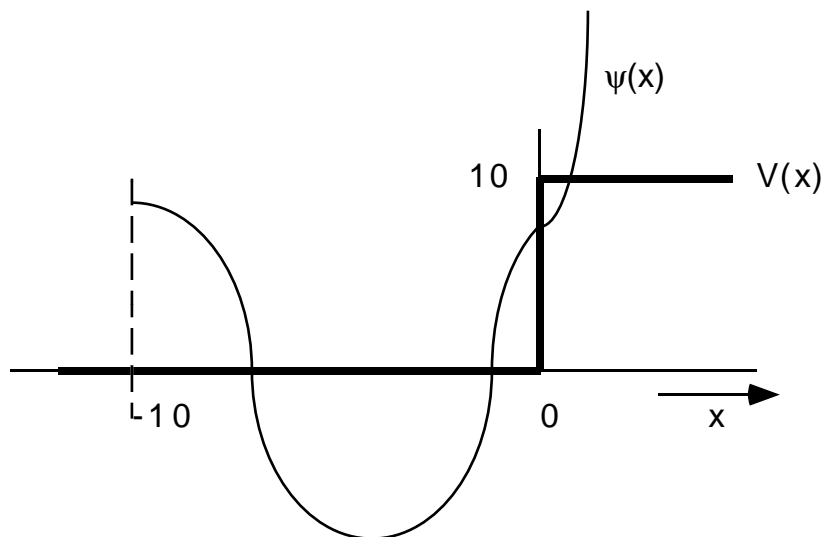


Figure 2: Step Potential showing a diverging wave-function.

Figure 2. What we have to look for is a solution where the wave-function decays to zero as it goes into the barrier.

In order to make a better behaved wave-function, the phase of the wave at the point when it hits the potential must be just right so that it dies away properly. A simple way of adjusting this phase is to adjust the initial phase at  $x = -10$  by giving  $d\psi/dx$  a non-zero value. Adjust this value appropriately until you get to a region where the wave-function decays neatly onto the x-axis. Now try extending the range of the calculation out to  $x = 3$ . You will probably find the wave-function starts to diverge again. More careful tuning of the inputs should stop the wave-function from blowing up at high  $x$ , but even after tuning, the approximation technique will eventually break down when you take the plot to even higher  $x$ . However by the time you have tuned the wave to die down to  $x = 3$ , you should have a good idea what the ideal wave-function looks like. *Note down the shape of the wave-function and how far it penetrates into the potential barrier.*

Now you have a good solution to the Schrödinger Equation, try doubling the initial values (both  $\psi$  and  $d\psi/dx$ ). *Describe what you see, and explain the significance of the amplitude of the wave-function.*

Try repeating the exercise with a different energy (remembering to keep  $E < 10$  for the moment). Good values to try out are 5, 9.5 — do not waste time by trying to tune the parameters to several decimal places, after all, this is only an approximation method. With the higher energies, you should calculate the wave-function out to higher values of  $x$  — with  $E = 9.5$  you should plot the wave-function all the way out to  $x = 10$ . *Note down the differences observed in the shape of the wave-function before and after the barrier as the energy increases.*

You should have done enough by now to convince yourself that for all energies up to  $E = 10$  (*i.e.* the height of the barrier), with a carefully selected phase of the wave, a stable wave-function is always possible. Finally try making  $E > 10$  and *comment on the result*.

## 1.2 Particle Colliding with a Barrier (Optional)

In wave mechanics, particles are described by the superposition of many wave-functions to form ‘wave packets’. In week 2 you saw how such a wave packet can be formed by summing a number of cosines with slightly different frequencies. To describe a particle hitting a barrier we have to sum over many of the individual solutions of the Schrödinger equation for the step potential.

You have already seen what the individual solutions look like, so this time you will use the analytical solutions. You may like to check that these look similar to your earlier results. Eigenfunctions of the time-independent Schrödinger equation for a step potential at  $x = 0$  are of the form:

$$\begin{aligned}\psi(x, k) &= \frac{1}{\sqrt{V_0}} \left[ k \cos kx - (\sqrt{V_0 - k^2}) \sin kx \right] && \text{for } x \leq 0 \\ &= \frac{1}{\sqrt{V_0}} k e^{-(\sqrt{V_0 - k^2})x} && \text{for } x > 0\end{aligned}\quad (11)$$

where  $V_0$  is the size of the potential step and  $k$  is the wave number of the function for negative  $x$ . Time dependency is included by multiplying by  $\exp(-iEt) = \exp(-ik^2t)$  to give the full wave-function

$$\Psi(x, t) = \psi(x) e^{-ik^2t}. \quad (12)$$

Create a wave packet by summing eigenfunctions with amplitude

$$G(k) = e^{-9(k-2)^2} e^{ik^26} \quad (13)$$

with  $k = 1, 1.05 \dots 3$ . (The complex factor in  $G(k)$  is needed to place the wave packet a short distance away for the barrier at  $t = 0$ .) Use a potential step of  $V_0 = 10$  and plot the probability density  $\Psi^*(x, t)\Psi(x, t)$  over the range  $-60 < x < 10$ . Animate the plot over the time range  $0 < t < 16$  and describe the phenomena you observe.

## 2 Potential Wells

### 2.1 The Finite Square Well

Another interesting set of solutions to the Schrödinger Equation are the bound states of a particle confined in a potential well. In this case, only discrete energies lead to stable solutions of the Schrödinger Equation, leading to a spectrum of bound states. This exercise will illustrate how this comes about.

Analytical solutions for particles trapped in an infinite well are easily obtained, since the wave-functions are just sine-waves fitting into the well in a similar way to vibrations on a string. However, if the well is finite (*i.e.* the energy,  $E$ , is of similar magnitude, to the potential difference,  $V$ , between the bottom and top of the well), then the solutions are more difficult to calculate and even more so for unusually shaped potentials. This is where a numerical solution becomes useful.

A suitable potential well for this problem is defined below:

$$\begin{aligned} V(x) &= 16 && \text{for } |x| > 1 \\ &= 0 && \text{for } |x| \leq 1 \end{aligned} \tag{14}$$

To start with we will be looking for the lowest energy state, and you can assume that this state,  $\psi(x)$ , will be an even function, since we have used a potential that is symmetric about  $x = 0$ . The potential and a possible lowest energy state are illustrated in Figure 3. Therefore you need only look at the solution for  $x \geq 0$ , and assume the other half will be the mirror image. This is shown by the ‘Region of Simulation’ in Figure 3. Also this gives us the clue that we should start by looking for a solution with  $d\psi/dx = 0$  at  $x = 0$ . The magnitude of the wave-function is arbitrary, so you can start with any positive value of  $\psi$  at  $x = 0$ .

Write a worksheet to display the shape of  $\psi(x)$  over the range  $0 \leq x \leq 2$ . Start with an Energy,  $E$ , of 1. As in the case of the step potential, you are looking for a wave-function that tends to zero as it penetrates into the potential barrier. Again, the solution needs to be finely tuned, and even so will eventually inflate to infinity because of the inaccuracy of the approximation. The only parameter you have free to tune in this example is the energy. As you reach a good solution, you should extend your calculation range out to  $x = 4$ , and re-tune the energy as before. By doing this you should find a well behaved wave-function corresponding to the lowest energy solution, and be able to measure its energy. *Note down this energy.* As before, do not bother with many decimal places - this is only an approximate method anyway.

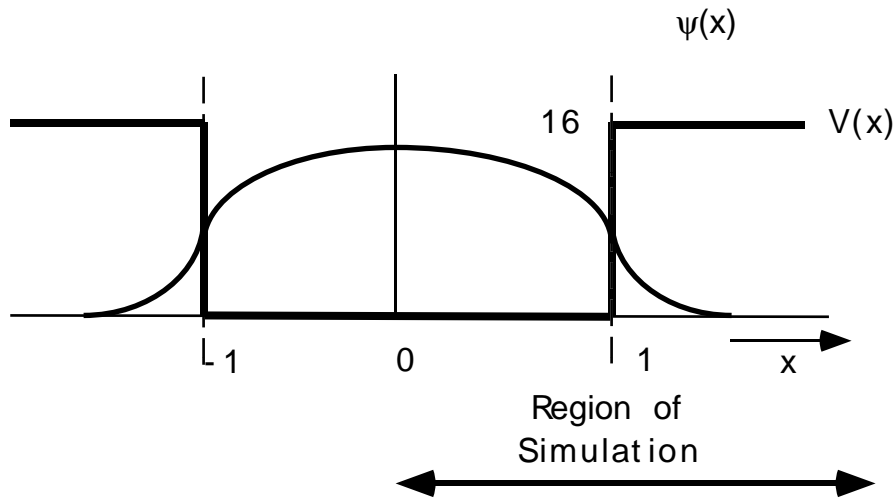


Figure 3: Square Potential Well showing shape of lowest energy solution and region of simulation.

We would like to show that a solution only exists for certain energies. That is, a particle trapped in a potential well has characteristic quantum levels. In order to justify this statement, try finding a solution for  $E = 1.7$ . By comparison with the first exercise, we could adjust the phase of the initial values by setting  $d\psi/dx$  as a non-zero value. Try doing this in order to find a solution that dies away in the usual way as  $x$  gets larger. *When you have done this, explain why this actually isn't a stable solution to the problem.*

For the potential well given, there are actually 2 more stable bound energy levels. Look for these other solutions, concentrating on energies around 6 and 13, and *note down the final energies*. However, before trying this, think about what shape you expect these second and third energy levels to have, because it might have some implications for your initial conditions.

Finally try an energy  $E > 16$ . *Describe what you see, and comment on it.*

## 2.2 The Quantum Harmonic Oscillator

It is instructive to look at the quantum version of the harmonic oscillator. This can be done easily by changing the potential used in the last section. This time we require a quadratic potential — the simple equation given below is suitable:

$$V(x) = x^2 \tag{15}$$

You can now try the same sort of experimentation with the energy as above until you find some bound states. You should extend the range of the calculation out to whatever value seems necessary to show that you have found a stable solution. You should look for both odd and even functions. *Try looking at the first few energy*

levels, and show that the energy of successive levels is given by:

$$E = (2n + 1) \quad \text{where } n = 0, 1, 2, \dots$$

*Having observed these numbers, compare them to your knowledge of the Quantum Harmonic Oscillator from theory.*

As stated at the start, since we are ignoring certain constants, we can say little about the absolute magnitude of the energy levels. To do this would only be a matter of putting in real values for  $\hbar$ ,  $m$ . Nevertheless, we have still managed to demonstrate the basic structure of the energy levels of a quantum harmonic oscillator.

### 3 The Hydrogen Atom (Optional)

The final example extends the Schrödinger Equation to three dimensions in showing the solutions for a single electron in orbit of a Hydrogen nucleus. You may have seen some of the analytical solution for this situation, but it is far too complex to cover in this class. Here we will give you the form of the wave-functions, and you will be able to explore exactly what they look like using Mathcad's graph plotting functions.

The stationary states of the hydrogen atom can be found by solving the time independent Schrödinger equation using the method of separation of variables. The spatial dependence of the electron wave-function in spherical polar coordinates can be written

$$\psi_{nlm_l}(r, \theta, \phi) = R_{nl}(r)Y_{lm_l}(\theta, \phi) \quad (16)$$

where  $n$  is known as the principal quantum number,  $l$  is the angular momentum quantum number and  $m_l$  is the magnetic quantum number. Each wave-function with a unique set of  $(n, l, m_l)$  values can accommodate two electrons, one with spin up and one with spin down. We will consider the radial wave-functions  $R_{nl}(r)$  and angular wave-functions  $Y_{lm_l}(\theta, \phi)$  separately, but remember that it is their product that gives the electron wave-function  $\psi_{nlm_l}$ .



$n$	$l$	$R_{nl}(r)$
1	0	$\left(\frac{Z}{a_0}\right)^{3/2} \cdot 2 \exp\left(-\frac{Zr}{a_0}\right)$
2	0	$\left(\frac{Z}{2a_0}\right)^{3/2} \cdot 2 \left(1 - \frac{1}{2} \frac{Zr}{a_0}\right) \exp\left(-\frac{1}{2} \frac{Zr}{a_0}\right)$
2	1	$\left(\frac{Z}{2a_0}\right)^{3/2} \cdot \frac{1}{\sqrt{3}} \frac{Zr}{a_0} \exp\left(-\frac{1}{2} \frac{Zr}{a_0}\right)$
3	0	$\left(\frac{Z}{3a_0}\right)^{3/2} \cdot 2 \left(1 - \frac{2}{3} \frac{Zr}{a_0} + \frac{2}{27} \left(\frac{Zr}{a_0}\right)^2\right) \exp\left(-\frac{1}{3} \frac{Zr}{a_0}\right)$
3	1	$\left(\frac{Z}{3a_0}\right)^{3/2} \cdot \frac{8\sqrt{2}}{9} \frac{Zr}{a_0} \left(1 - \frac{1}{6} \frac{Zr}{a_0}\right) \exp\left(-\frac{1}{3} \frac{Zr}{a_0}\right)$
3	2	$\left(\frac{Z}{3a_0}\right)^{3/2} \cdot \frac{2\sqrt{2}}{27\sqrt{5}} \left(\frac{Zr}{a_0}\right)^2 \exp\left(-\frac{1}{3} \frac{Zr}{a_0}\right)$

Table 1: Radial Wave-functions,  $R_{nl}(r)$ . These functions are normalised so that the integrated probability density is 1. That is:  $\int r^2 R_{nl}^2 dr = 1$ .

## Radial Wave-Functions

The first few  $R_{nl}$  are listed in Table 1, where for the hydrogen atom the atomic number  $Z = 1$ . In addition to  $R_{nl} = 0$  at  $r = 0$  and  $r = \infty$ , there are  $n - l - 1$  other zeros of these wave-functions. To a first approximation, in zero applied magnetic field, the electron energy depends only on  $n$ . (The fact that it does not depend on  $l$  is a consequence of the spatial dependence of the Coulomb potential.) The energy levels are

$$E_n = -\frac{1}{2} \left( \frac{e^2}{4\pi\epsilon_0 a_0} \right) \frac{1}{n^2} \quad (17)$$

where  $a_0 = 4\pi\epsilon_0\hbar/m_e^2$ ; this is the Bohr radius and equals 0.053 nm.

For a particular value of  $n$ , the allowed values of  $l$  are in the range  $0, 1 \dots (n-1)$ . For each value of  $l$  there are  $(2l+1)$  values of  $m_l$  in the range  $-l, -l+1 \dots l-1, l$ . (The physical interpretations of  $l$  and  $m_l$  are discussed below.) For fixed  $n$ , states with different  $l$  and  $m_l$  have the same energy since  $E_n$  depends on  $n$  only (i.e. they are *degenerate*.) The number of degenerate states is given by  $2\sum_{l=0}^{n-1} (2l+1) = 2n^2$ , where the prefactor of 2 is included to account for the effects of electron spin. In spectroscopic notation, the  $n$ -states with  $l = 0, 1, 2, 3$  are called  $ns, np, nd, nf$  respectively.

The ground state of the hydrogen atom has  $n = 1$ ,  $l = 0$  and  $m_l = 0$ , and is non-degenerate, but it can be occupied by two electrons of opposite spins; this is the  $1s$  state. The states of the next highest energy have  $n = 2$ ,  $l = 0$  and  $1$ , and therefore an overall degeneracy of 4 (there are 8 separate states with  $n = 2$  if we include the effects of electron spin); these are the  $2s$  (one of them, with  $l = 0$  and  $m_l = 0$ ) and  $2p$  states (three of them, with  $l = 1$  and  $m_l = -1, 0, +1$ ). For  $n = 3$ , we have the states  $3s$  (one,  $l = 0$ ),  $3p$  (three,  $l = 1$ ) and  $3d$  (five,  $l = 2$ ), so the  $n = 3$  “shell” can accommodate a total of 18 electrons. We can continue this process for larger values of  $n$ .

## Angular Wave-Functions

The first few of these are listed in Table 2, and are often called spherical harmonics  $Y_{lm_l}$ . As described above, for fixed  $n$  all of these wave-functions have the same energy. However, each wave-function with a separate value of  $l$  has a different electron angular momentum equal to  $\sqrt{l(l+1)}\hbar$ , with a component of this about any specified direction of  $m_l\hbar$ ; this is the physical interpretation of  $l$  and  $m_l$ . Each spherical harmonic with angular momentum quantum number  $l$  has  $(2l+1)$  degenerate states, each with their own value of  $m_l$  (with  $-l \leq m_l \leq l$ ).

For  $ns$  states,  $l = 0$  and  $m_l = 0$ , and the angular part of wave-function is  $Y_{0,0}$ . For  $np$  states the situation is more complex since there are three of them, each with their own directionality in space. It is conventional to take the  $np_z$  state as  $Y_{1,0}$ . However, the wave-functions  $Y_{1,1}$  and  $Y_{1,-1}$  do not have the same shape as  $Y_{1,0}$ . For convenience, the states  $np_x$  and  $np_y$  are formed from linear combinations of  $Y_{1,1}$  and  $Y_{1,-1}$  that result in similar shapes to  $np_z$ , except that they are directional along the  $x$  and  $y$  axes respectively. A list of the linear combinations for these and the  $nd$  states can be found in Table 3. Whether we create these linear combinations of  $Y_{lm_l}$  or just work with the isolated spherical harmonics depends on the context; the linear combinations are more convenient for discussing the bonding in molecules, while the individual  $Y_{lm_l}$  are more appropriate for isolated atoms.

## Exercises

The radial and angular wave-functions of Tables 1–3 have been provided for you. This will save much tedious typing and bug-fixing. They are located on the hard disk as the file ‘C:\Winmcd\Course4\Hydrogen.mcd’. It is assumed  $Z = 1$  for the Hydrogen Atom. All you are required to do is plot them and study their shape. Print out some of the graphs you generate, but there is no need to print out the functions! In the case of the angular wave-functions, it will be necessary to use a new surface plotting technique, known as Parametric Surface Plots. It is described on page 498 of the Mathcad Manual.

$l$	$m_l$	$Y_{lm_l}(\theta, \phi)$
0	0	$\frac{1}{\sqrt{4\pi}}$
1	1	$-\sqrt{\frac{3}{8\pi}} \sin \theta \exp(i\phi)$
1	0	$\sqrt{\frac{3}{4\pi}} \cos \theta$
1	-1	$\sqrt{\frac{3}{8\pi}} \sin \theta \exp(-i\phi)$
2	2	$\sqrt{\frac{15}{32\pi}} \sin^2 \theta \exp(2i\phi)$
2	1	$-\sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta \exp(i\phi)$
2	0	$\sqrt{\frac{15}{16\pi}} (3 \cos^2 \theta - 1)$
2	-1	$\sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta \exp(-i\phi)$
2	-2	$\sqrt{\frac{15}{32\pi}} \sin^2 \theta \exp(-2i\phi)$

Table 2: Angular Wave-functions (Spherical Harmonics),  $Y_{l,m_l}(\theta, \phi)$ . These functions are normalised so that the integrated probability density is 1. That is:  $\int \int |Y_{lm_l}|^2 d\theta d\phi = 1$ .

$$\begin{aligned}
s &= Y_{0,0} \\
p_x &= \frac{-i}{\sqrt{2}}(Y_{1,1} + Y_{1,-1}) \\
p_y &= \frac{-1}{\sqrt{2}}(Y_{1,1} - Y_{1,-1}) \\
p_z &= Y_{1,0} \\
d_{xy} &= \frac{-i}{\sqrt{2}}(Y_{2,2} - Y_{2,-2}) \\
d_{xz} &= \frac{-i}{\sqrt{2}}(Y_{2,1} + Y_{2,-1}) \\
d_{yz} &= \frac{-1}{\sqrt{2}}(Y_{2,1} - Y_{2,-1}) \\
d_{x^2-y^2} &= \frac{-1}{\sqrt{2}}(Y_{2,2} + Y_{2,-2}) \\
d_{z^2} &= Y_{2,0}
\end{aligned}$$

Table 3: The ‘physical’ s, p and d electron shells expressed in terms of the spherical harmonics.

1. Plot the radial wave-functions  $R_{nl}(r)$  and radial probability density  $r^2 R_{nl}^2(r)$  as a function of  $r/a_0$  for the wave-functions listed in Table 1. Check that the number of nodes of  $R_{nl}(r)$  is  $n - l - 1$ .
2. The probability of finding an electron within a distance of the nucleus in the  $R_{nl}$  state is given by

$$P(\rho) = \int_0^\rho r^2 R_{nl}^2(r) dr \quad (18)$$

and when  $\rho/a_0$  becomes very large,  $P(\rho)$  is close to 1. Plot  $P(\rho)$  for a few of the radial wave-functions.

3. Plot some of the angular probabilities  $s^2, p_z^2, d_{xy}^2, \dots$ , for a few of the wave-functions listed in Table 2. You will need to convert spherical polar coordinates  $(r, \theta, \phi)$  into Cartesian coordinates  $(x, y, z)$ . The formulae for this are:

$$\begin{aligned}
x &= r \sin(\theta) \cos(\phi) \\
y &= r \sin(\theta) \sin(\phi) \\
z &= r \cos(\theta)
\end{aligned} \quad (19)$$