# Lectures 15-20

## Outline:

1. **Introduction to Partial differential equations.**
2. **The Wave equation.**
3. **The Shrödinger equation.**
4. **The 2D Laplace equation.**
5. **The Diffusion equation.**
6. **The 3D coordinate systems.**
7. **The Spherical harmonics.**

Note: The rest of this course is *not* covered by Jordan & Smith. These notes are complete although you may find the Course Pack helpful.

## Introduction to PDEs

In many physical situations we encounter quantities which depend on two or more variables, for example the displacement of a string varies with space and time: $y(x, t)$. Handing such functions mathematically involves *partial differentiation* and *partial differential equations* (PDEs).

### Revision of Partial Differentiation

Consider a function $y(x, t)$. Remember that to find $\frac{\partial y}{\partial x}$ (the partial derivative of $y$ with respect to $x$), we differentiate with respect to $x$ treating $t$ as a constant.

*Example* Let $y = x^2 \sin t$. So $\frac{\partial y}{\partial x} = 2x\sin t$, $\frac{\partial y}{\partial t} = x^2 \cos t$, $\frac{\partial^2 y}{\partial x^2} = 2\sin t$ and $\frac{\partial^2 y}{\partial t^2} = -x^2 \sin t$.

### Partial Differential Equations

Some of the most commonly occuring PDEs, and their areas of application, are listed below:

| | | | |
|---|---|---|---|
| 1 | $\nabla^2 u = \frac{1}{c^2}\frac{\partial^2 u}{\partial t^2}$ | Wave equation | Elastic waves, sound waves, electromagnetic waves, etc. |
| 2 | $-\frac{\hbar^2}{2m}\nabla^2 u + Vu = i\hbar\frac{\partial u}{\partial t}$ | Schrödinger's equation | Quantum mechanics |
| 3 | $\nabla^2 u = \frac{1}{h^2}\frac{\partial u}{\partial t}$ | Diffusion equation | Heat flow, chemical diffusion, etc. |
| 4 | $\nabla^2 u = 0$ | Laplace's equation | Electromagnetism, gravitation, hydrodynamics, heat flow. |
| 5 | $\nabla^2 u = -\frac{\rho}{\varepsilon_0}$ | Poisson's equation | As (4) in regions containing mass, charge, sources of heat, etc. |

Remember from last year that Gauss equation relates the surface integral of the electric field to the charge inside the surface. This can also be written as $\nabla \cdot E = \frac{\rho}{\varepsilon_0}$ and since the electric field is related to the potential by $E = -\nabla V$ then we can write $\nabla^2 V = -\frac{\rho}{\varepsilon_0}$. This is Poisson's equation, and in a charge free region of space this becomes Laplace's equation. This can be directly applied to fluid flow or gravitation by reassigning terms. The Schrödinger and diffusion equations will be covered in future lectures.

---

We will start by looking at equations 1-3 in one space dimension, then move on to 3D problems.

In many cases, solutions of PDEs can be found by separation of the variables. We will learn this method by considering waves on strings. In subsequent lectures we will use a similar procedure to solve many other PDEs.

## The One-Dimensional Wave Equation

*See Course Pack p.69-74, 95-101.*

Waves on strings are governed by the equation $\frac{\partial^2 y(x,t)}{\partial x^2} = \frac{1}{c^2}\frac{\partial^2 y(x,t)}{\partial t^2}$, where $y(x, t)$ is the displacement of the string at position $x$ and time $t$.

You have met this equation briefly in Y1 and learned that $c^2 = T/\mu$, where $\mu$ is the mass per unit length of the string, $T$ is the tension, and $c$ is the wave velocity. In this course we will not be concerned with where the equation came from but only with finding its solutions, i.e. determining the motion of the string.

Consider the specific case of a string of length $L$ attached at both ends to rigid supports. Then we additionally have the boundary conditions $y(0, t) = y(L, t) = 0$.

*Note:* A PDE can *never* be solved without knowing the boundary conditions!

**Step 1: Separation of the Variables**

Our boundary conditions are true at special values of $x$ and for *all* values of time.

Looking at the boundary conditions we can notice that the conditions should be satisfied for specific values of $x$ but for all times $t$. This means that the solution can be factorised: $y(x,t) = X(x)T(t)$, where functions denoted by capital letters $X$ and $T$ are functions of $x$ and $t$ respectively.

Substituting this into the wave equation:

We have $\frac{\partial^2 y}{\partial x^2} = \frac{\partial^2}{\partial x^2}\left[X(x)T(t)\right] = T(t)\frac{d^2X(x)}{dx^2}$ and similarly $\frac{1}{c^2}\frac{\partial^2 y}{\partial t^2} = \frac{1}{c^2}X(x)\frac{d^2T(t)}{dt^2}$.

So substitution gives $T(t)\frac{d^2X(x)}{dx^2} = \frac{X(x)}{c^2}\frac{d^2T(t)}{dt^2}$.

Rearrange the equation so all the terms in $x$ are on one side and all the terms in $t$ are on the other:

$$\frac{1}{X(x)}\frac{d^2X(x)}{dx^2} = \frac{1}{c^2T(t)}\frac{d^2T(t)}{dt^2}$$

The *only* way this can be satisfied for all $x$ and $t$ is if *both* sides are equal to a constant:

$$\frac{1}{X(x)}\frac{d^2X(x)}{dx^2} = \frac{1}{c^2T(t)}\frac{d^2T(t)}{dt^2} = \text{constant}.$$

Suppose we call the constant $N$.

Then we have $\frac{1}{X(x)}\frac{d^2X(x)}{dx^2} = N$ which rearranges to $\frac{d^2X(x)}{dx^2} = N\,X(x)$. (1)

And $\frac{1}{c^2T(t)}\frac{d^2T(t)}{dt^2} = N$ which rearranges to $\frac{d^2T(t)}{dt^2} = Nc^2\,T(t)$. (2)

Now we have *ordinary differential equations* for $X(x)$ and $T(t)$ – which we can solve.

Consider the equation for $X(x)$. Previously we have looked at two similar equations (assuming that $N \neq 0$):

(i) $\frac{d^2}{dt^2}X(t) + \omega_0^2 X(t) = 0$ Linear harmonic oscillator

(ii) $\frac{d^2}{dt^2}X(t) - \alpha^2 X(t) = 0$ Unstable equilibrium

*Which case we have depends on whether our constant N is positive or negative. We need to make an appropriate choice for N by considering the physical situation, particularly the boundary conditions.*

**Step 2: Satisfying the Boundary Conditions**

In our case the boundary conditions are $y(0, t) = y(L, t) = 0$. This means $X(0) = X(L) = 0$, i.e. $X$ is equal to zero at *two* different points. This is crucial in determining the sign of $N$. Remember that (i) has oscillatory solutions (meaning that it will pass through zero displacement many times), whilst the solutions of (ii) are exponential growth and decay that only tend to $x = 0$ once (see previous lectures and compare a pendulum with a pencil falling from the vertical). In other words:

$N \neq 0$, otherwise the solution for $X(x)$ is $X(x) = ax + b$; the boundary conditions would require then that $a = 0$ and $b = 0$ and hence, $X \equiv 0$ – not interesting.

If $N$ is positive, let's say $N = k^2$, then $X(x) = Ae^{kx} + Be^{-kx}$ and again to satisfy the boundary conditions, $A = B = 0$, and hence $X \equiv 0$.

So $N$ should be negative. Let's take $N = -k^2$.
So (1) becomes $\frac{d^2X(x)}{dx^2} = -k^2 X(x)$. This has a general solution $X(x) = A\cos kx + B\sin kx$.

Now we apply the boundary conditions:

$X(0) = 0$ gives $A = 0$.

We must take $B \neq 0$. So $X(L) = 0$ requires $\sin kL = 0$, i.e. $kL = n\pi$.
So $k$ can only take certain values $k_n = n\pi / L$ where $n$ is an integer (which we can chose to be positive)

So we have $X_n(x) = B_n \sin\frac{n\pi x}{L}$ for $n = 1, 2, 3, \ldots$.

The equations for $X(x)$ and $T(t)$ are equal to the *same* constant, so equation (2) becomes

$$\frac{d^2T(t)}{dt^2} = Nc^2 T(t) = -k^2 c^2 T(t).$$

Looking at the diagram below $\lambda_n = \frac{2L}{n}$ and since $k_n = \frac{2\pi}{\lambda_n}$ then $k_n = \frac{n\pi}{L}$.

Since $c$ is the wave velocity and $c = f\lambda$, we can write $c = \frac{\omega\lambda}{2\pi} = \frac{\omega}{k}$ and so $\omega_n = k_n c = \frac{n\pi c}{L}$.

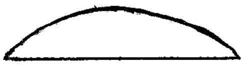
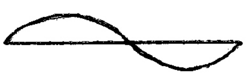
So we can say that $\frac{d^2T(t)}{dt^2} = -\omega_n{}^2\, T(t)$. This again has the form of the LHO equation.

Therefore it has solutions of the form $T_n(t) = (Ce^{i\omega_n t} + De^{-i\omega_n t})$ or $T_n(t) = (C\sin\omega_n t + D\cos\omega_n t)$ or $T_n(t) = C\cos(\omega_n t + \phi_n)$.

Hence we have solutions:

$$y_n(x,t) = X_n(x)T_n(t) = B_n \sin k_n x \cos(\omega_n t + \phi_n) = B_n \sin\frac{n\pi x}{L}\cos\left(\frac{n\pi ct}{L} + \phi_n\right).$$

We see that each $y_n$ represents harmonic motion with a different wavelength (different frequency). In the diagram below of course time is constant (as it's a photo not a movie!!):

| | | | | | |
|---|---|---|---|---|---|
| $n = 1$ |  | Fundamental | $k_1 = \frac{\pi}{L}$, | $\lambda_1 = \frac{2\pi}{k_1} = 2L$, | $\omega_1 = \frac{\pi c}{L}$ |
| $n = 2$ |  | 2nd harmonic | $k_2 = 2k_1 = \frac{2\pi}{L}$, | $\lambda_2 = \frac{\lambda_1}{2} = L$, | $\omega_2 = \frac{2\pi c}{L} = 2\omega_1$ |
| $n = 3$ |  | 3rd harmonic | $k_3 = 3k_1 = \frac{3\pi}{L}$, | $\lambda_3 = \frac{\lambda_1}{3} = \frac{2}{3}L$, | $\omega_3 = 3\omega_1$, etc. |

### The Superposition Principle

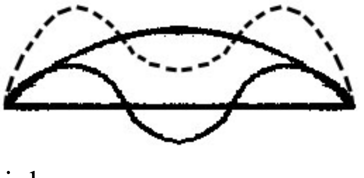
The wave equation (and all PDEs which we will consider) is a *linear* equation, meaning that the dependent variable and all its derivatives appear to the 1st power. For such equations there is a fundamental theorem called the **superposition principle**, which states that *if* $y_1$ *and* $y_2$ *are solutions of the equation then* $y = c_1 y_1 + c_2 y_2$ *is also a solution, for any constants* $c_1, c_2$. Put more simply this means that the net amplitude caused by two or more waves traversing the same space, is the sum of the amplitudes which would have been produced by the individual waves separately. Although this principle has been mainly used to describe constructive and destructive interference of waves, it was also used last year to describe net voltage within a circuit, energy transfer along a bar heated at both ends, and in the summation of the effects of charge distribution.

### Step 3: Constructing the General Solution

Bearing in mind the superposition principle, the general solution of our equation is the sum of all solutions: $y(x,t) = \sum_{n=1}^{\infty} B_n \sin\frac{n\pi x}{L}\cos\left(\frac{n\pi ct}{L} + \phi_n\right)$.

This is the most general answer to the problem. For example, if a skipping rope was oscillated at both its fundamental frequency and its 3rd harmonic, then the rope would look like the dashed line at some specific point in time and generally its displacement could be described by the equation :-

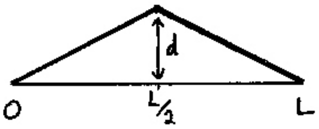
$$y(x,t) = B_1 \sin\frac{\pi x}{L}\cos\left(\frac{\pi ct}{L} + \phi_1\right) + B_3 \sin\frac{3\pi x}{L}\cos\left(\frac{3\pi ct}{L} + \phi_3\right)$$



NB. The Fourier series is a further example of the superposition principle.

### Step 4: Solution of Complete Problem using Fourier Series

Suppose we have been given further information, namely we have been told that at time $t = 0$ the string is released from rest in the configuration shown below:



At $t = 0$ the string is at rest, i.e. $\left.\frac{\partial y}{\partial t}\right|_{t=0} = 0$, if we differentiate we find

$\frac{\partial y}{\partial t} = \sum_{n=1}^{\infty} -\frac{B_n n\pi c}{L}\sin\frac{n\pi x}{L}\sin\left(\frac{n\pi ct}{L} + \phi_n\right) = 0$ so for this to be true $\phi_n = 0$ for all $n$.

So the general solution becomes $y(x,t) = \sum_{n=1}^{\infty} B_n \sin\frac{n\pi x}{L}\cos\frac{n\pi ct}{L}$.

So at time $t = 0$, $y(x,0) = \sum_{n=1}^{\infty} B_n \sin\frac{n\pi x}{L}$.

If we look back to the lectures on Fourier series. we will see that the coefficients $B_n$ are the coefficients of the Fourier series for the given initial configuration! We've already shown that the configuration drawn above at $t = 0$ can be expressed as a half-range sine series,

$B_n = \frac{2}{L}\int_0^L f(x)\sin\frac{n\pi x}{L}dx$, where $f(x)$ is the function that determines the string deviation at the initial time (see figure). In our case the solution at $t = 0$ becomes (see previous lectures on Fourier series):

$$y(x,0) = \frac{8d}{\pi^2}\left[\sin\frac{\pi x}{L} - \frac{1}{9}\sin\frac{3\pi x}{L} + \frac{1}{25}\sin\frac{5\pi x}{L} - \frac{1}{49}\sin\frac{7\pi x}{L} + \ldots\right] \quad \text{for } 0 \le x \le L.$$

Hence, by trusting the superposition principle and therefore treating each harmonic as a separate oscillating sinusoidal waveform, we deduce that at later times the configuration of the string will be:-

$$y(x,t)=\frac{8d}{\pi^2}\left[\sin\frac{\pi x}{L}\cos\frac{\pi ct}{L}-\frac{1}{9}\sin\frac{3\pi x}{L}\cos\frac{3\pi ct}{L}+\frac{1}{25}\sin\frac{5\pi x}{L}\cos\frac{5\pi ct}{L}-\frac{1}{49}\sin\frac{7\pi x}{L}\cos\frac{7\pi ct}{L}+\ldots\right].$$

**SUMMARY** of the procedure used:

1. We have an equation $\frac{\partial^2 y(x,t)}{\partial x^2}=\frac{1}{c^2}\frac{\partial^2 y(x,t)}{\partial t^2}$ with boundary conditions $y(0,t)=y(L,t)=0$.
   We look for a solution of the form $y(x,t)=X(x)T(t)$.
   We find that the variables can be separated $\frac{1}{X(x)}\frac{d^2X(x)}{dx^2}=\frac{1}{c^2T(t)}\frac{d^2T(t)}{dt^2}=N$
2. We use the boundary conditions to deduce that $N$ must be negative, i.e. $N=-k^2$.
   We use the boundary conditions further to find the allowed values of $k$ and hence find $X(x)$.
   We find the corresponding solution of the equation for $T(t)$.
   Hence we can write down the solutions of the PDE.
3. By the principle of superposition, the general solution is a sum over all solutions.
4. Given the initial conditions, or similar information, the Fourier series can be used to find the solution that satisfies initial conditions.

Later on we will use a similar procedure to solve other PDEs.

## The Schrödinger Equation

Consider the time dependent Schrödinger equation in 1 dimensional space:

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2}+V(x,t)\Psi(x,t)=i\hbar\frac{\partial\Psi(x,t)}{\partial t}.$$

In a region of zero potential, $V(x,t)=0$, this simplifies to:

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2}=i\hbar\frac{\partial\Psi(x,t)}{\partial t}.$$

Let us solve this subject to boundary conditions $\Psi(0,t)=\Psi(L,t)=0$ (as for the *infinite potential well*).

**Step 1: Separation of the Variables**

Our boundary conditions are true at special values of $x$, for *all* values of time, so we look for solutions of the form $\Psi(x,t)=X(x)T(t)$. Substitute this into the Schrödinger equation:

$$-\frac{\hbar^2}{2m}\frac{d^2X(x)}{dx^2}T(t)=i\hbar X(x)\frac{dT(t)}{dt}$$

Multiply both sides by $\frac{1}{X(x)Y(y)}$: $$-\frac{\hbar^2}{2m}\frac{1}{X}\frac{d^2X}{dx^2}=\frac{i\hbar}{T}\frac{dT}{dt}$$

Now we have separated the variables. The above equation can only be true for all $x$, $t$ if both sides are equal to a constant. It is conventional (for good reasons – see below and PHY202!) to call the constant $E$.

So we have $-\frac{\hbar^2}{2m}\frac{1}{X}\frac{d^2X}{dx^2}=E$ which rearranges to $\frac{d^2X}{dx^2}=-\frac{2mE}{\hbar^2}X.$ (3)

And $\frac{i\hbar}{T}\frac{dT}{dt}=E$ which rearranges to $\frac{dT}{dt}=-\frac{iE}{\hbar}T.$ (4)

**Step 2: Satisfying the Boundary Conditions**

**For *X*(*x*)**

Our boundary conditions are $\Psi(0,t)=\Psi(L,t)=0$, which means $X(0)=X(L)=0$.

So clearly we need $E > 0$, so that equation (1) has the form of the harmonic oscillator equation.

It is simpler to rewrite (1) as $\dfrac{d^2X}{dx^2} = -k^2X$, where $k^2 = \dfrac{2mE}{\hbar^2}$, i.e. $E = \dfrac{\hbar^2k^2}{2m}$.

Then the general solution for $X(x)$ is $X(x) = A\cos kx + B\sin kx$.

Apply the boundary conditions: $X(0) = 0$ gives $A = 0$; we must have $B \neq 0$ so $X(L) = 0$ requires

$\sin kL = 0$, i.e. $k_n = n\pi/L$, so $X_n(x) = B_n \sin\dfrac{n\pi x}{L}$ for $n = 1, 2, 3, \ldots$.

**For *T*(*t*)**

Equation (4) has solution $T = T_0 e^{-iEt/\hbar}$ (See first order ODEs).

So we have solutions: $\Psi_n(x,t) = X_n(x)T_n(t) = B_n \sin\dfrac{n\pi x}{L}\, e^{-iE_nt/\hbar}$, where $E_n = \dfrac{\hbar^2 k_n^{\,2}}{2m} = \dfrac{n^2\hbar^2\pi^2}{2mL^2}$.

(These are the *energy eigenstates* of the system.)

**Step 3: Constructing the General Solution**

Hence the general solution is $\Psi(x,t) = \sum_{n=1}^{\infty} \Psi_n(x,t) = \sum_{n=1}^{\infty} B_n \sin\dfrac{n\pi x}{L} \exp(-iE_nt/\hbar)$.

(In general therefore a particle will be in a *superposition* of eigenstates.)

**Step 4: Solution of Complete Problem**

If we know the state of the system at $t = 0$, we can find the state at any later time.

For example, suppose that $\Psi(x,0) = \sqrt{\dfrac{2}{L}}\left[\dfrac{1}{\sqrt{2}}\sin\dfrac{\pi x}{L} + \dfrac{1}{\sqrt{2}}\sin\dfrac{2\pi x}{L}\right]$. Then we can deduce that

$$\Psi(x,t) = \sqrt{\frac{2}{L}}\left[\frac{1}{\sqrt{2}}\sin\frac{\pi x}{L}\exp(-iE_1t/\hbar) + \frac{1}{\sqrt{2}}\sin\frac{2\pi x}{L}\exp(-iE_2t/\hbar)\right], \text{ where } E_1 = \frac{\hbar^2\pi^2}{2mL^2},\ E_2 = \frac{4\hbar^2\pi^2}{2mL^2}.$$

---

## The Laplace Equation in 2D

We now start looking at the diffusion equation, $\nabla^2 u = \dfrac{1}{h^2}\dfrac{\partial u}{\partial t}$. One physical phenomenon governed by this equation is heat flow. That is, in many situations, $T(x, y, z, t)$ satisfies $\nabla^2 T = \dfrac{1}{h^2}\dfrac{\partial T}{\partial t}$. In 'steady state' problems where nothing is changing with time, the equation simplifies to $\nabla^2 T = 0$, which is the Laplace equation. (This can be applied to electrostatics if the temperatures were replaced by potentials.) We will look at this equation in 2D by considering the following exercises

*Exercise 1*

*Consider a rectangular metal plate 10 cm wide and very long. The two long sides and the far end are held at 0°C and the base at 100°C. Find the steady state temperature distribution inside the plate. NB. You will need to use the superposition principle at the end to satisfy the boundary conditions!!*

Our PDE is $\nabla^2 T = \dfrac{\partial^2 T}{\partial x^2} + \dfrac{\partial^2 T}{\partial y^2} = 0$.

**Step 1: Separation of the variables – look for solutions in the form *T*(*x*, *y*) = *X*(*x*)*Y*(*y*).**

So substituting gives $Y(y)\dfrac{\partial^2 X(x)}{\partial x^2} + X(x)\dfrac{\partial^2 Y(y)}{\partial y^2} = 0$ and dividing through by $X(x)Y(y)$ we get :

$$\frac{1}{X(x)}\frac{\partial^2 X(x)}{\partial x^2}+\frac{1}{Y(y)}\frac{\partial^2 Y(y)}{\partial y^2}=0 \quad \text{and so} \quad \frac{1}{X(x)}\frac{\partial^2 X(x)}{\partial x^2}=-\frac{1}{Y(y)}\frac{\partial^2 Y(y)}{\partial y^2}$$

**Step 2: Satisfy the boundary conditions. Considering the BCs, choose the appropriate constant of separation. Find the general forms of *X*(*x*) and *Y*(*y*). Apply relevant BCs. Find the solutions.**

Now we set both sides equal to a constant. When choosing the constant we must think carefully about the boundary conditions. We know that $X(0) = X(L) = 0$ and we know that in the $Y$ direction we expect an exponential drop or something similar from $T(x, 0) = 100$ to $T(x,\infty) = 0$. Think back again to the LHO solution and the falling pencil solution for 2nd order ODEs. It is clear now that for a solution in $x$ such that $X(x) = 0$ more than once, the constant must be negative (like a LHO). For convenience we choose the constant as $-k^2$ so….

$$\frac{1}{X(x)}\frac{\partial^2 X(x)}{\partial x^2}=-\frac{1}{Y(y)}\frac{\partial^2 Y(y)}{\partial y^2}=-k^2$$

So $\frac{\partial^2 X(x)}{\partial x^2}=-k^2X(x)$ and $\frac{\partial^2 Y(y)}{\partial y^2}=k^2Y(y)$ with solutions

$$X(x)=A\cos kx+B\sin kx \quad \text{and} \quad Y(y)=Ce^{-ky}+De^{ky}$$

Now we must again think of the boundary conditions and attempt to deduce $A$, $B$, $C$ and $D$. We know that $X(0) = X(L) = 0$ and if this is true then $A = 0$. Also since $X(L) = 0 = B \sin kx$ then $kL = n\pi$ so we can say $X(x)=B\sin\frac{n\pi x}{L}$. Now looking at $Y(y)=Ce^{-ky}+De^{ky}$ and since we know that $T(x,y) \to 0$ as $y\to\infty$ then we can state that $D = 0$ and $Y(y)=Ce^{-ky}$.

So solutions are $T(x,y)=Ce^{-ky}B\sin\frac{n\pi x}{L}=CBe^{\frac{-n\pi y}{L}}\sin\frac{n\pi x}{L}=Pe^{\frac{-n\pi y}{10}}\sin\frac{n\pi x}{10}$ if $P = CB$ and $L = 10$.

**Step 3: Construct the general solution.**

So the general solution can be written as $T(x,y)=\sum_{n=1}^{\infty}P_n e^{\frac{-n\pi y}{L}}\sin\frac{n\pi x}{L}=\sum_{n=1}^{\infty}P_n e^{\frac{-n\pi y}{10}}\sin\frac{n\pi x}{10}$

This already satisfies the boundary conditions for $x$, namely that $T(0, y) = T(L, y) = 0$. All that remains is to calculate the required values of $P$ such that the $T(x, 0) = 100$ is satisfied.

**Step 4: Use the remaining information to solve the complete problem. (Fourier series is useful.)**

Since the temperature at $y = 0$ is 100, then

$$T(x,0)=\sum_{n=1}^{\infty}P_n e^{\frac{-n\pi 0}{L}}\sin\frac{n\pi x}{L}=\sum_{n=1}^{\infty}P_n\sin\frac{n\pi x}{L}=\sum_{n=1}^{\infty}P_n\sin\frac{n\pi x}{10}=100.$$

Here is a lateral jump that isn't obvious!!!! Remember from previous lectures that the half-range sine series is a sum of sine terms that can represent things like plucked guitar strings. Look how similar this is to the expression for $T(x, 0)$ if we set $L = 10$ and $f(x) = 100$.

**Half-range sine series**: $f(x)=\sum_{n=1}^{\infty}b_n\sin\frac{n\pi x}{L}$, where $b_n=\frac{2}{L}\int_0^L f(x)\sin\frac{n\pi x}{L}dx$.

So all we have to do now is calculate the half-range sine series in the usual way.

$$P_n=\frac{2}{L}\int_0^L f(x)\sin\frac{n\pi x}{L}dx=\frac{2}{10}\int_0^{10}100\sin\frac{n\pi x}{10}dx=-20\left[\frac{10}{n\pi}\cos\frac{n\pi x}{10}\right]_0^{10}=\frac{-200}{n\pi}\left(\cos\frac{10n\pi}{10}-\cos 0\right)$$

$$P_n = \frac{-200}{n\pi}\left(\cos\frac{10n\pi}{10} - \cos 0\right) = \frac{-200}{n\pi}\left(\cos n\pi - 1\right)$$

So in order for the boundary conditions for $T(x, 0) = 100$ to be satisfied, we must take the following values of $P_n$ in the sum.

| $n$ | $P_n$ |
|---|---|
| 1 | $\frac{-200}{\pi}\left(-1-1\right) = \frac{400}{\pi}$ |
| 2 | $\frac{-200}{2\pi}(1-1) = 0$ |
| 3 | $\frac{-200}{3\pi}(-1-1) = \frac{400}{3\pi}$ |

Finally we can state the full solution that satisfies initial conditions:

$$T(x,y) = \sum_{n=1}^{\infty} P_n e^{\frac{-n\pi y}{10}} \sin\frac{n\pi x}{10} = \sum_{n=1}^{n=\infty\ odd} \frac{400}{\pi n}\left(e^{\frac{-n\pi y}{10}} \sin\frac{n\pi x}{10}\right)$$

# The Diffusion Equation

*References*: Course Pack p.64-69, 102-107.

In classical physics, almost all time dependent phenomena may be described by the wave equation or the diffusion equation. At the micro and nanometre scale, diffusion is often the dominant phenomenon.

The 1D diffusion equation has the form $\frac{\partial^2 F(x,t)}{\partial x^2} = \frac{1}{D}\frac{\partial F(x,t)}{\partial t}$.

$F$ is the quantity that diffuses. It is usually a concentration, for example the concentration of a chemical diffusing through a region, the concentration of particles in a liquid, the concentration of defects in a solid, concentration of spin densities, etc.

$D$ is the diffusion constant. $D$ has dimensions [length]$^2$/[time], i.e. units m$^2$ s$^{-1}$.

Heat conduction also obeys this situation. $F$ is then temperature, $T$. And many books write $D = h^2 = \frac{K}{\rho C}$, where $h^2$ is the thermal diffusivity of the material, which depends on the thermal conductivity $K$, the density $\rho$ and the specific heat of the material $C$. (For metals, typically $h^2 \sim 1\times10^{-4}$ m$^2$ s$^{-1}$.)

So we have the heat flow equation $\frac{\partial^2 T(x,t)}{\partial x^2} = \frac{1}{h^2}\frac{\partial T(x,t)}{\partial t}$.

We will study heat flow because it is a concept familiar from daily life but the same mathematics can be applied to many other diffusion situations.

## Thermal Relaxation of a rod with ends held at 0°C

Consider a perfectly insulated rod of length $L$. Both ends are held at temperature 0ºC at all times.
At time $t = 0$, the temperature distribution along the rod has a given function $T(x, 0) = f(x)$.

**Step 1.** Our differential equation is $\frac{\partial^2 T(x,t)}{\partial x^2} = \frac{1}{h^2}\frac{\partial T(x,t)}{\partial t}$.

Look for solutions of the form $T(x,t) = X(x)\theta(t)$.

Substituting this into the PDE gives $\frac{d^2 X(x)}{dx^2}\theta(t) = \frac{1}{h^2}X(x)\frac{d\theta(t)}{dt}$.

Multiply both sides by $\frac{1}{X(x)\theta(t)}$: $\frac{1}{X(x)}\frac{d^2 X(x)}{dx^2} = \frac{1}{h^2}\frac{1}{\theta(t)}\frac{d\theta(t)}{dt}$.

To be true at all $x$, $t$, both sides of the above equation must be equal to a constant.

**Step 2.** Since we are told in the boundary conditions that both ends of the rod are held at 0°C at all times we choose a negative constant, $-k^2$, to give LHO type solutions, and rearrange to get two ODEs:

$\frac{d^2X(x)}{dx^2} = -k^2X$ which has general solution $X(x) = A\cos kx + B\sin kx$

$\frac{d\theta(t)}{dt} = -k^2h^2\theta(t)$ which has general solution $\theta(t) = Ce^{-k^2h^2t}$

We have T(0, $t$) = T($L$, $t$) = 0, so $X(0) = X(L) = 0$, so (similar to previous problems) $A = 0$, $B = n\pi / L$.

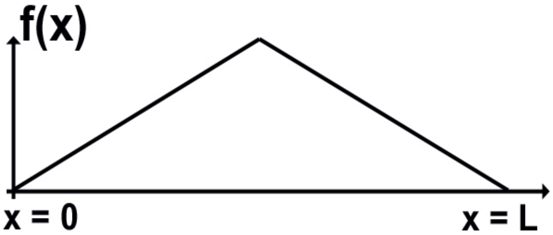
So we have solutions $T_n(x,t) = X(x)\theta(t) = B_n \sin\frac{n\pi x}{L} e^{-\frac{t}{\tau_n}}$, where $\tau_n = \frac{1}{h^2k^2} = \left(\frac{L}{n\pi h}\right)^2$.

**Step 3.** The general solution therefore is $T(x,t) = \sum_n T_n(x,t) = \sum_n B_n \sin\frac{n\pi x}{L} e^{-\frac{t}{\tau_n}}$.

**Step 4.** At time $t = 0$, the temperature distribution is $T(x, 0) = f(x)$, so $T(x,0) = \sum_n B_n \sin\frac{n\pi x}{L} = f(x)$.

Thus the coefficients $B_n$ are the coefficients of the half-range Fourier sine series of the function $f(x)$.

Let's say that the temperature distribution along the rod at $t = 0$ is triangular.



$f(x) = x$ for $0 < x < L/2$

$f(x) = -x + L$ for $L/2 < x < L$

**i.e. temperature midway in °C is equal to half distance in m.**

**Half-range sine series expression**: $f(x) = \sum_{n=1}^{\infty} b_n \sin\frac{n\pi x}{d}$, where $b_n = \frac{2}{d}\int_0^d f(x)\sin\frac{n\pi x}{d}dx$.

Here $d = L$,

So $b_n = \frac{2}{L}\int_0^L f(x)\sin\frac{n\pi x}{L}dx = \frac{2}{L}\int_0^{L/2} x\sin\frac{n\pi x}{L}dx + \frac{2}{L}\int_{L/2}^{L}(L-x)\sin\frac{n\pi x}{L}dx$

$\int x\sin\frac{n\pi x}{L}dx$ is found by parts set $u = x$ so $du = dx$ set $dv = \sin\frac{n\pi x}{L}dx$ so $v = -\frac{L}{n\pi}\cos\frac{n\pi x}{L}$

So $\int x\sin\frac{n\pi x}{L}dx = -\frac{Lx}{n\pi}\cos\frac{n\pi x}{L} + \int \frac{L}{n\pi}\cos\frac{n\pi x}{L}dx = -\frac{Lx}{n\pi}\cos\frac{n\pi x}{L} + \frac{L^2}{n^2\pi^2}\sin\frac{n\pi x}{L}$

So $b_n = \frac{2}{L}\left[-\frac{Lx}{n\pi}\cos\frac{n\pi x}{L} + \frac{L^2}{n^2\pi^2}\sin\frac{n\pi x}{L}\right]_0^{L/2} + \frac{2}{L}\int_{L/2}^{L} L\sin\frac{n\pi x}{L}dx + \frac{2}{L}\left[\frac{Lx}{n\pi}\cos\frac{n\pi x}{L} - \frac{L^2}{n^2\pi^2}\sin\frac{n\pi x}{L}\right]_{L/2}^{L}$

$$b_n = \frac{2}{L}\left[-\frac{L^2}{2n\pi}\cos\frac{n\pi}{2} + \frac{L^2}{n^2\pi^2}\sin\frac{n\pi}{2}\right] - 2\left[\frac{L}{n\pi}\cos\frac{n\pi x}{L}\right]_{L/2}^{L} + \frac{2}{L}\left[\frac{L^2}{n\pi}\cos n\pi - \frac{L^2}{2n\pi}\cos\frac{n\pi}{2} + \frac{L^2}{n^2\pi^2}\sin\frac{n\pi}{2}\right]$$

$$b_n = \left[-\frac{L}{n\pi}\cos\frac{n\pi}{2} + \frac{2L}{n^2\pi^2}\sin\frac{n\pi}{2}\right] - 2\left[\frac{L}{n\pi}\cos n\pi - \frac{L}{n\pi}\cos\frac{n\pi}{2}\right] + \left[\frac{2L}{n\pi}\cos n\pi - \frac{L}{n\pi}\cos\frac{n\pi}{2} + \frac{2L}{n^2\pi^2}\sin\frac{n\pi}{2}\right]$$

$$b_n = \frac{4L}{n^2\pi^2}\sin\frac{n\pi}{2}$$

| | | | |
|---|---|---|---|
| $n=1,\ b_1=\frac{4L}{\pi^2}$ | $n=2,\ b_2=0$ | $n=3,\ b_3=-\frac{4L}{3^2\pi^2}=-\frac{4L}{9\pi^2}$ | $n=4,\ b_4=0$ |

So $b_n=\frac{4L}{n^2\pi^2}$ for $n=1,\ 5,\ 9$ and $b_n=-\frac{4L}{n^2\pi^2}$ for $n=3,\ 7,\ 11$

**Half-range sine series is written**: $f(x)=\sum_{n=1}^{\infty} b_n \sin\frac{n\pi x}{d}$, so here $f(x)=\sum_{n=1}^{\infty}\frac{4L}{n^2\pi^2}\sin\frac{n\pi}{2}\sin\frac{n\pi x}{L}$

**Step 5.** At time $t = 0$, the temperature distribution is $T(x, 0) = f(x)$, so $T(x,0)=\sum_{n=1} B_n\sin\frac{n\pi x}{L}=f(x)$

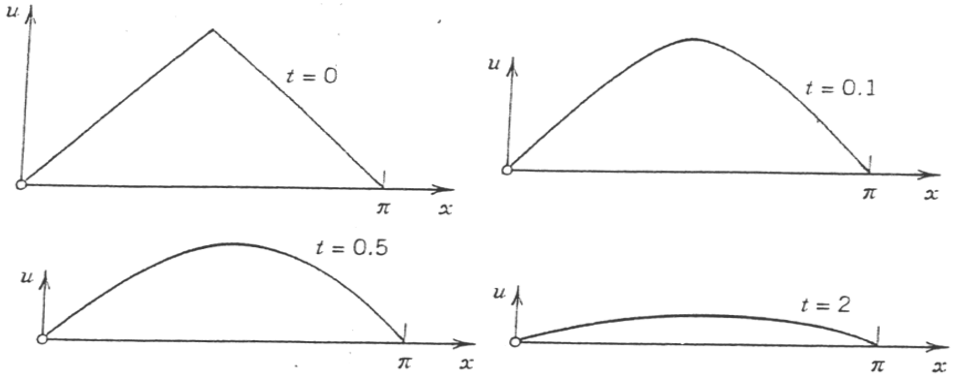
Therefore comparing terms $B_n=\frac{4L}{n^2\pi^2}\sin\frac{n\pi}{2}$.

**Step 6.** The full solution for the rod is therefore:

$$T(x,t)=\sum_n B_n\sin\frac{n\pi x}{L}e^{-\frac{t}{\tau_n}}=\sum_{n=1}^{\infty}\frac{4L}{n^2\pi^2}\sin\frac{n\pi}{2}\sin\frac{n\pi x}{L}e^{-\frac{t}{\tau_n}},\quad \text{where}\quad \tau_n=\frac{1}{h^2k^2}=\left(\frac{L}{n\pi h}\right)^2$$

$$T(x,t)=\frac{4L}{\pi^2}\left[\frac{1}{1}\sin\frac{\pi x}{L}e^{-\frac{\pi^2h^2t}{L^2}}-\frac{1}{9}\sin\frac{3\pi x}{L}e^{-\frac{9\pi^2h^2t}{L^2}}+\frac{1}{25}\sin\frac{5\pi x}{L}e^{-\frac{25\pi^2h^2t}{L^2}}-.....\right]$$

Now we have all the boundary conditions, we can stick in appropriate values of $h$ and find how the temperature profile drops over time. It can be shown that $T(x, t)$ with increasing time looks like this:



Notice how the fundamental frequency lasts the longest.

## Thermal relaxation of an isolated body

In the last example the ends of rod were immersed in a massive reservoir at 0°C so that heat was able to continually flow out of the rod. Now imagine that the ends are insulated just like the rest of the rod. Imagine we start at time = 0 with the same triangular temperature distribution as before. With time, the temperature distribution will become uniform. The temperature of the body will then be at some non zero temperature.

The rate of heat flow is known to be proportional to the temperature gradient $\frac{\partial T(x,t)}{\partial x}$.

The body being isolated means there is no heat flow out of the ends so at $x = 0$ and $x = L$,

$\left.\frac{\partial T(x,t)}{\partial x}\right|_{x=0} = \left.\frac{\partial T(x,t)}{\partial x}\right|_{x=L} = 0$. Applying these boundary solutions to the general solution for $X(x)$ we find

that since, $X(x) = A\cos kx + B\sin kx$ then $\left.\frac{\partial T(x,t)}{\partial x}\right|_{x=0} = \left.\frac{dX(x)}{dx}\right|_{x=0} = -Ak\sin kx + Bk\cos kx$.

Therefore $0 = -Ak\sin k0 + Bk\cos k0$ and so $0 = B$

and $0 = -Ak\sin kL + Bk\cos kL$ and so $0 = -Ak\sin kL$ and therefore $kL = n\pi$ or $k = \frac{n\pi}{L}$.

Putting this back into expression for $X(x)$ we find $X(x) = A\cos kx = A_n\cos\frac{n\pi x}{L}$.

Therefore following the same steps as above we find the solutions and the corresponding general solution having the respective forms:

$$T_n(x,t) = A_n\cos(n\pi x/L)e^{-t/\tau_n} \quad \text{and} \quad T(x,t) = \sum_n T_n(x,t) = \sum_n A_n\cos\frac{n\pi x}{L}e^{-\frac{t}{\tau_n}}.$$

We are therefore left with the cosine rather than the sine terms in the expression and so we must solve the half range <u>COSINE</u> series for the temperature function $f(x)$.

**Half-range cosine series**: $f(x) = \frac{1}{2}a_0 + \sum_{n=1}^{\infty} a_n\cos\frac{n\pi x}{L}$, where $a_n = \frac{2}{L}\int_0^L f(x)\cos\frac{n\pi x}{L}\,dx$.

This can be shown to give coefficients: $a_0 = \frac{L}{2}$ and $a_n = \frac{2L}{n^2\pi^2}\left(2\cos\frac{n\pi}{2} - \cos n\pi - 1\right)$,

giving $f(x) = \frac{L}{4} + \sum_{n=1}^{\infty}\frac{2L}{n^2\pi^2}\left(2\cos\frac{n\pi}{2} - \cos n\pi - 1\right)\cos\frac{n\pi x}{L}$.

| | | | | |
|---|---|---|---|---|
| $n = 1$,<br>$a_1 = 0$ | $n = 2,\ a_2 = \frac{2L}{2^2\pi^2}(-4) = \frac{-8L}{2^2\pi^2}$ | $n = 3$,<br>$a_3 = 0$ | $n = 4$,<br>$a_4 = 0$ | $n = 5$,<br>$a_5 = 0$ |

$$n = 6, \quad a_6 = \frac{2L}{6^2\pi^2}\left(2\cos 3\pi - \cos 6\pi - 1\right) = \frac{2L}{6^2\pi^2}(-4) = \frac{-8L}{6^2\pi^2}$$

Comparison with the general solution at time = 0 i.e. $T(x,0) = \sum_n T_n(x,0) = \sum_n A_n\cos\frac{n\pi x}{L}$ allows the coefficients $A_n$ to be determined.

The full solution then:

$$T(x,t) = \sum_n A_n\cos\frac{n\pi x}{L}e^{-\frac{t}{\tau_n}} = \frac{L}{4} - \frac{8L}{\pi^2}\left\{\frac{1}{2^2}\cos\frac{2\pi x}{L}e^{-\frac{2^2h^2\pi^2t}{L^2}} + \frac{1}{6^2}\cos\frac{6\pi x}{L}e^{-\frac{6^2h^2\pi^2t}{L^2}} + \ldots.\right\}.$$

Notice that as t → ∞, $\left(e^{-\frac{n^2h^2\pi^2t}{L^2}}\right) \to 0$ and so $T(x,\infty) = \frac{L}{4}$ This is the final uniform temperature of the rod.

<u>Concluding Summary</u>

1. Sinusoidal functions of $x$ are solutions of the diffusion equation. Hence Fourier methods are again useful. (In fact Fourier actually invented them to solve heat flow problems.)
2. The temperature distribution decays exponentially with time.

3. The time constant of the decay is proportional to $k^{-2}$, i.e. to $\lambda^2$ and therefore also $L^2$. So the longest wavelengths (such as the fundamental) last longest.
4. Hence if we write an initial temperature distribution as a Fourier series, normally the first term is the most important in determining the behaviour at later times.

- **Importance of $\tau \propto \lambda^2$.**

To see points 3&4 more clearly, we can rewrite $T(x,t) = \sum_n T_n(x,t) = \sum_n B_n \sin\frac{n\pi x}{L}\exp(-n^2 t/\tau_1)$

where $\tau_1$ is the relaxation time of the 'fundamental' $n = 1$ term, $\tau_n = \left(\frac{L}{h\pi}\right)^2$.

After a time $t = \tau$, for example, the n$^{\text{th}}$ term has decayed by a factor $\exp(-n^2)$. Looking at values for this for $n = 1, 2, 3, \ldots$ below, we can see that the higher modes decay very fast indeed:

| | |
|---|---|
| $e^{-1}$ | 0.37 |
| $e^{-4}$ | 0.02 |
| $e^{-9}$ | $1.2\times10^{-4}$ |
| $e^{-16}$ | $1.1\times10^{-7}$ |
| $e^{-25}$ | $1.4\times10^{-11}$ |
| $e^{-36}$ | $2.3\times10^{-16}$ |
| $e^{-49}$ | $5.3\times10^{-22}$ |

To know exactly how the temperature profile changes with time then we need all the terms. But usually a very good approximation can be obtained by considering just the first term.

- **Importance of $\tau \propto L^2$**

We are used to thinking of time scaling linearly with distance. For example, if it takes us 20 mins to walk a mile it takes 40 mins to walk 2 miles etc. But 'diffusion time' scales with the *square* of the length. Values of $h^2$ vary between $\sim 1\times10^{-4}$ m$^2$ s$^{-1}$ for a metal and $\sim 1\times10^{-7}$ m$^2$ s$^{-1}$ for cork.

So using $\tau_n = \left(\frac{L}{n\pi h}\right)^2$ from previous page in 1 second, heat travels a distance of very approximately $L \approx \pi h$, which is ~3 cm for a metal, ~1 mm for cork.

*On an everyday scale.* If food is cut up smaller it cooks faster! (Cookery books tell you the cooking time scales as the weight (= length$^3$), but actually it scales as the square of the thinnest dimension!)

*On the large scale.* Why don't we heat up because of the earth's core? The heat must travel through about 30 km of sand and gravel. Taking the diffusion constant for this material to be $h^2 \sim 1\times10^{-6}$ m$^2$ s$^{-1}$, we have $\tau \sim L^2/\pi^2 h^2 \sim 10^{14}$ seconds $\sim 10^6$ years.

*On the small scale.* Chemical diffusion constants for ions in water, $D$, are of the order of $D \sim 10^{-9}$ m$^2$ s$^{-1}$ where $D = h^2$. Our bodies function because ions can diffuse in and out of our muscle cells, acting as switches. The time taken for ions to diffuse across a cell of width L= $10^{-6}$ m is $\tau \sim L^2/\pi^2 D \sim 10^{-4}$ seconds, which is suitably quick. Could humans be scaled up so our cells were 1 cm across and still function? No! Because the time would then be $\tau \sim L^2/\pi^2 D \sim 10^4$ seconds which is too slow!

# 3D Coordinate Systems

*References*: Course Pack p.121-123, 131-146.

## 3D Cartesian Coordinates

We can describe all space using coordinates (*x, y, z*), each variable ranging from -∞ to +∞.

### 1. PDEs in 3D Cartesian Coordinates

Consider the wave equation. In one dimensional space we had $\frac{\partial^2\Psi(x,t)}{\partial x^2}=\frac{1}{c^2}\frac{\partial^2\Psi(x,t)}{\partial t^2}$.

This can be generalised to 2D (see Course Pack p.111-117) and 3D.

In 3D the wave equation becomes $\frac{\partial^2\Psi(x,y,z,t)}{\partial x^2}+\frac{\partial^2\Psi(x,y,z,t)}{\partial y^2}+\frac{\partial^2\Psi(x,y,z,t)}{\partial z^2}=\frac{1}{c^2}\frac{\partial^2\Psi(x,y,z,t)}{\partial t^2}$,

which may be written also as $\nabla^2\Psi(x,y,z,t)=\frac{1}{c^2}\frac{\partial^2\Psi(x,y,z,t)}{\partial t^2}$.

Let us look for a solution of the form $\Psi(x,y,z,t)=X(x)Y(y)Z(z)T(t)$, i.e. we try to separate the variables, as done in 1D. Differentiating gives

$$\frac{\partial^2\Psi(x,y,z,t)}{\partial x^2}=Y(y)Z(z)T(t)\frac{d^2X}{dx^2},\quad \text{and similarly}\quad \frac{\partial^2\Psi(x,y,z,t)}{\partial y^2}=X(x)Z(z)T(t)\frac{d^2Y}{dy^2},$$

$$\frac{\partial^2\Psi(x,y,z,t)}{\partial z^2}=X(x)Y(y)T(t)\frac{d^2Z}{dz^2},\qquad \frac{\partial^2\Psi(x,y,z,t)}{\partial t^2}=X(x)Y(y)Z(z)\frac{d^2T}{dt^2}.$$

Substituting these into the PDE then dividing through by $\Psi(x,y,z,t)=X(x)Y(y)Z(z)T(t)$, we get

$$\frac{1}{X(x)}\frac{d^2X(x)}{dx^2}+\frac{1}{Y(y)}\frac{d^2Y(y)}{dy^2}+\frac{1}{Z(z)}\frac{d^2Z(z)}{dz^2}=\frac{1}{c^2T(t)}\frac{d^2T(t)}{dt^2}.\qquad (*)$$

Each term in this expression is a function of only *one* variable. In order for the equation to hold for all *x, y, z* and *t*, each term must equal a constant. We want a *wave* solution to the wave equation, i.e. harmonic terms, so we choose each term to equal a *negative* constant. We let

$$\frac{1}{T(t)}\frac{d^2T(t)}{dt^2}=-\omega^2,\qquad \frac{1}{X(x)}\frac{d^2X(x)}{dx^2}=-k_x{}^2,\qquad \frac{1}{Y(y)}\frac{d^2Y(y)}{dy^2}=-k_y{}^2,\qquad \frac{1}{Z(z)}\frac{d^2Z(z)}{dz^2}=-k_z{}^2.$$

Comparing with equation (*) we see that the constants, ω, $k_x$, $k_y$, $k_z$ are related by $\frac{\omega^2}{c^2}=k_x^2+k_y^2+k_z^2=k^2$.

Each of the ODEs above has the normal harmonic solutions, which we can write in terms of sines and cosines below. (The bracketed layout simply means that each variable can be represented either by sine or cosine depending on the boundary conditions and must not be confused with matrices).

$$X(x)\sim\begin{Bmatrix}\sin k_xx\\ \cos k_xx\end{Bmatrix},\quad Y(y)\sim\begin{Bmatrix}\sin k_yy\\ \cos k_yy\end{Bmatrix},\quad Z(z)\sim\begin{Bmatrix}\sin k_zz\\ \cos k_zz\end{Bmatrix},\quad T(t)\sim\begin{Bmatrix}\sin\omega t\\ \cos\omega t\end{Bmatrix}.$$

Giving special solutions of the form $\Psi(x,y,z,t)=A\begin{Bmatrix}\sin k_xx\\ \cos k_xx\end{Bmatrix}\begin{Bmatrix}\sin k_yy\\ \cos k_yy\end{Bmatrix}\begin{Bmatrix}\sin k_zz\\ \cos k_zz\end{Bmatrix}\begin{Bmatrix}\sin\omega t\\ \cos\omega t\end{Bmatrix}$.

Or sometimes it is more convenient to use complex exponentials,

$$X(x)\sim e^{\pm ik_xx},\qquad Y(y)\sim e^{\pm ik_yy},\qquad Z(z)\sim e^{\pm ik_zz},\qquad T(t)\sim e^{\pm i\omega t}.$$

Then we get solutions such as

$$\Psi(x,y,z,t)=A\exp(i\omega t-ik_xx-ik_yy-ik_zz)=A\exp(i\omega t-i\,\mathbf{k}\cdot\mathbf{r}),\qquad \text{where } \mathbf{k}=k_x\hat{\mathbf{i}}+k_y\hat{\mathbf{j}}+k_z\hat{\mathbf{k}}.$$

As we might have expected, the solutions are plane waves with wavevector **k** (which is also the direction of travel of the wave) and frequency $\omega=ck$.

A general solution can then be written as a sum over all solutions, and applying boundary conditions we can determine which terms contribute and the allowed values of $k_x$, etc.

For example, suppose we have a box with dimensions $L_1$, $L_2$, $L_3$ in the $x$, $y$, $z$ directions respectively and know that $\Psi$ must vanish at the walls. Then the solutions will be:

$$\Psi(x,y,z,t) = A\sin k_x x \, \sin k_y y \, \sin k_z z \, \sin \omega t, \text{ where } k_x = \frac{n_1\pi}{L_1}, \; k_y = \frac{n_2\pi}{L_2}, \; k_z = \frac{n_3\pi}{L_3}.$$

So each solution, or 'mode' will be characterized by *three* integers, $n_1$, $n_2$, $n_3$.

And this mode will have angular frequency $\omega^2 = c^2(k_x{}^2 + k_z{}^2 + k_z{}^2) = \pi^2c^2\left(\frac{n_1{}^2}{L_1{}^2} + \frac{n_2{}^2}{L_2{}^2} + \frac{n_3{}^2}{L_3{}^2}\right)$.

An important question which arises in various areas of physics is the question of how many different modes (i.e. unique combinations of integers $n_1$, $n_2$, $n_3$) exist in a given frequency range, or in the frequency interval $\omega$ to $\omega + d\omega$? The answer is central to the derivation of Planck's Law for blackbody radiation, the Debye theory of heat capacities of solids, and various other situations.

### 2. Integrals in 3D Cartesian Coordinates

We have $dV = dx\,dy\,dz$, and must perform a triple integral over $x$, $y$ and $z$. Normally we will only choose to work in Cartesian coordinates if the region over which we are to integrate is cuboid or comprises all space. Integrating over spherical regions, for example, is very nasty in Cartesian coordinates!

***Example***

*Find the 3D Fourier transform,* $F(\mathbf{k}) = \frac{1}{(2\pi)^{3/2}} \iiint\limits_{all\,space} f(\mathbf{r}) e^{-i\mathbf{k}\cdot\mathbf{r}} dV$, *of* $f(x,y,z) = \begin{cases} 1, & |x| < a, |y| < b, |z| < c \\ 0, & otherwise \end{cases}$.

The integral is just the product of three 1D integrals, and is thus easily evaluated:

$$F(k_x,k_y,k_z) = \frac{1}{(2\pi)^{3/2}} \int_{-a}^{a} e^{-ik_x x} dx \int_{-b}^{b} e^{-ik_y y} dy \int_{-c}^{c} e^{-ik_z z} dz = \frac{1}{(2\pi)^{3/2}} \left(\frac{e^{ik_x a} - e^{-ik_x a}}{ik_x}\right)\left(\frac{e^{ik_y b} - e^{-ik_y b}}{ik_y}\right)\left(\frac{e^{ik_z c} - e^{-ik_z c}}{ik_z}\right)$$

This is therefore a product of three *sinc* functions, i.e. $\left(\frac{e^{ik_x a} - e^{-ik_x a}}{ik_x}\right) = \frac{2\sin(k_x a)}{k_x} = 2a \; \text{sinc}(k_x a)$.

So doing this for all three components we get:

$$F(k_x,k_y,k_z) = \frac{8}{(2\pi)^{3/2}} \frac{\sin(k_x a)}{k_x} \frac{\sin(k_y b)}{k_y} \frac{\sin(k_z c)}{k_z} = \frac{8abc}{(2\pi)^{3/2}} \text{sinc}(k_x a)\,\text{sinc}(k_y b)\,\text{sinc}(k_z c).$$

Integrals of this sort are encountered in condensed matter physics in crystals with rectangular lattices.

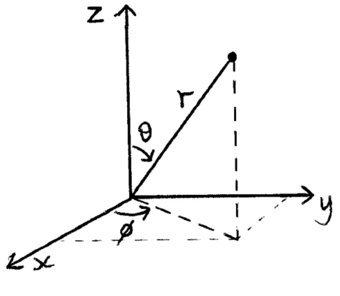
# 3D Spherical Polar Coordinates

### 1. Spherical Polar Coordinates: Revision

Spherical polar coordinates are the coordinate system of choice in almost all 3D problems. This is because most 3D objects are shaped more like spheres than cubes, e.g. atoms, nuclei, planets, etc.

Many potentials (Coulomb, gravitational, etc.) depend on $|\mathbf{r}| = \sqrt{x^2 + y^2 + z^2}$.

Physicists define $r$, $\theta$, $\phi$ as shown in the figure. They are related to Cartesian coordinates by $x = r\sin\theta\cos\phi$, $y = r\sin\theta\sin\phi$, $x = r\cos\theta$.



### 2. 3D Integrals in Spherical Polar Coordinates

The volume element is $dV = r^2 \sin\theta \, dr \, d\theta \, d\phi$ (given on data sheet).

To cover over all space, we take $0 \le r < \infty$, $0 \le \theta < \pi$, $0 \le \phi < 2\pi$.

### 3. $\nabla^2$ in Spherical Polar Coordinates: Spherical Solutions

As given on the data sheet, $\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$.

We'll look first at problems in which the solutions are known to be '*spherically symmetric*'. That is, the solutions depend on $r$, but have no angular dependence. They are functions of $r$ but not of $\theta$ or $\phi$.

For example if $F = F(r)$ then $\nabla^2 F(r) = \frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}F(r)\right)$.

**(a) The Laplace Equation** $\nabla^2 V(r) = 0$.

***Exercise*** *Find spherically symmetric solutions of Laplace Equation* $\nabla^2 V(r) = 0$.

We have $\nabla^2 V(r) = \frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}V(r)\right) = 0$.

In this case we can actually find $V(r)$ directly by rearranging and integrating, in steps.

Multiplying both sides by $r^2$ gives $\frac{d}{dr}\left(r^2\frac{d}{dr}V(r)\right) = 0$.

Integrating both sides gives $r^2\frac{d}{dr}V(r) = A$ where $A$ is a constant. This rearranges to $\frac{d}{dr}V(r) = \frac{A}{r^2}$.

Integrate both sides again and we get the general solution: $V(r) = -\frac{A}{r} + B$.

<u>*Application*</u>

In electrostatics we want a potential which vanishes at ∞, so set $B = 0$, then $V(r) = -\frac{A}{r}$.

This is the standard Coulomb potential from a point charge at the origin: $V(r) = \frac{Q}{4\pi\varepsilon_0 r}$, with $A = \frac{-Q}{4\pi\varepsilon_0}$.

We have demonstrated not only that the Coulomb potential satisfies Laplace's equation but that this is the *only* spherically symmetric solution.

**(b) The Wave Equation**

In 3D the wave equation is $\nabla^2\Psi = \frac{1}{c^2}\frac{\partial^2\Psi}{\partial t^2}$.

Let's only look for spherically symmetric solutions $\Psi(r,t)$, so the equation can be written

$$\nabla^2\Psi(r,t) = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi(r,t)}{\partial r}\right) = \frac{1}{c^2}\frac{\partial^2\Psi(r,t)}{\partial t^2}.$$

As previously we look for solutions of the form $\Psi(r,t) = R(r)T(t)$, substitute this back in the equation, and then separate the variables.

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{T(t)dR(r)}{dr}\right) = \frac{1}{c^2}\frac{R(r)d^2T(t)}{dt^2} \quad \text{gives} \quad \frac{1}{R(r)r^2}\frac{d}{dr}\left(r^2\frac{dR(r)}{dr}\right) = \frac{1}{c^2T(t)}\frac{d^2T(t)}{dt^2}$$

Each side of the equation must equal a constant, and we want oscillating solutions so we choose a negative constant. In order to help the maths let's set the constant as $-(\omega/c)^2$:

$$\frac{1}{R(r)r^2}\frac{d}{dr}\left(r^2\frac{dR(r)}{dr}\right) = \frac{1}{c^2T(t)}\frac{d^2T(t)}{dt^2} = -\left(\frac{\omega}{c}\right)^2$$

The equation for $T(t)$ is easy to solve. $\frac{d^2T(t)}{dt^2} = -c^2T(t)\left(\frac{\omega}{c}\right)^2 = -\omega^2T(t)$ giving $T(t) \sim e^{\pm i\omega t}$.

Now we need to solve $\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR(r)}{dr}\right) = -\left(\frac{\omega}{c}\right)^2 R(r) = -k^2R(r)$, (*)

where $k^2 = \frac{\omega^2}{c^2}$ .

Equations like this occur frequently. There is a standard trick which is to define $R(r) = \frac{u(r)}{r}$, solve for $u(r)$ and thus find $R(r)$.

Start by differentiating $R(r)$ with respect to $r$ using the product rule: $\frac{dR}{dr} = \frac{1}{r}\frac{du(r)}{dr} - u(r)\frac{1}{r^2}$.

Multiply both sides by $r^2$ gives $r^2\frac{dR}{dr} = r\frac{du(r)}{dr} - u(r)$.

Now differentiate again using the product rule. $\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) = r\frac{d^2u(r)}{dr^2} + \frac{du(r)}{dr} - \frac{du(r)}{dr} = r\frac{d^2u(r)}{dr^2}$

Therefore $\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR(r)}{dr}\right) = \frac{1}{r}\frac{d^2u(r)}{dr^2}$.

So equation (*) becomes: $\frac{1}{r}\frac{d^2u(r)}{dr^2} = -k^2\frac{u(r)}{r}$. The factors of $r$ cancel, giving $\frac{d^2u(r)}{dr^2} = -k^2u(r)$.

Thus we have solutions of the form:

$$u(r) = Ae^{ikr} + Be^{-ikr} \qquad R(r) = \frac{Ae^{ikr}}{r} + \frac{Be^{-ikr}}{r} \qquad \Psi(r,t) = R(r)T(t) = \frac{\left(Ae^{ikr} + Be^{-ikr}\right)}{r}e^{i\omega t}.$$

For waves moving out from the origin $\Psi(r,t) = \frac{Ae^{ikr}e^{i\omega t}}{r} = \frac{Ae^{i(kr+\omega t)}}{r}$.

For waves moving in towards the origin $\Psi(r,t) = \frac{Be^{-ikr}e^{i\omega t}}{r} = \frac{Be^{-i(kr-\omega t)}}{r}$

These are spherical waves moving in and out from the origin.
Note the factor of $1/r$. Intensity is related to amplitude squared. Our solution gives $|\Psi(r, t)|^2 \sim 1 / r^2$. This is the well known inverse square law.

Many other spherical equations and problems (e.g. heat flow in a sphere) can be solved in a similar way.

**Exercise 1** *Show by integration in spherical coordinates that a sphere of radius R has volume* $4\pi R^3/3$.

We have $V = \iiint_{sphere} r^2\sin\theta\, dr\, d\theta\, d\phi = \int_0^{2\pi} d\phi \int_0^{\pi}\sin\theta\, d\theta \int_0^{R} r^2 dr = [\phi]_0^{2\pi}\,[-\cos\theta]_0^{\pi}\left[\frac{r^3}{3}\right]_0^R = \frac{4\pi R^3}{3}$ .

**Exercise 2** *Find the Fourier transform of a screened Coulomb potential,* $U(r) = \frac{e^{-\lambda r}}{4\pi\varepsilon_0 r}$.

[This exercise is relevant to determining the scattering of electrons by a nucleus. The screening comes from the electrons bound in the atom. You will meet integrals like this in the Y3 nuclear physics module.]

As before we have the 3D Fourier transform $F(\mathbf{k}) = \frac{1}{(2\pi)^{3/2}}\iiint_{all\,space} f(\mathbf{r})e^{-i\mathbf{k}\cdot\mathbf{r}}dV$.

In this case $f(\mathbf{r}) = U(r)$ is a function only of the magnitude of $r$ and not its direction and so has perfect radial symmetry. Again the volume element is $dV = r^2 \sin\theta\, dr\, d\theta\, d\phi$ (given on data sheet).

We therefore have $F(\mathbf{k}) = \dfrac{1}{(2\pi)^{3/2}} \iiint\limits_{all\ space} U(r) e^{-i\mathbf{k}\cdot\mathbf{r}} \sin\theta\, dr\, d\theta\, d\phi$.

There is a standard 'trick' which is to choose the direction of **k** to be parallel to the polar (z) axis for the integral. Then **k·r** becomes $|k|\,|r| \cos\theta$. The whole integral is a function only of the magnitude of **k**, not its direction, i.e. $F(\mathbf{k})$ becomes $F(k)$:

$$F(k) = \frac{1}{(2\pi)^{3/2}} \iiint\limits_{all\ space} \frac{e^{-\lambda r}}{4\pi\varepsilon_0 r} e^{-ikr\cos\theta} r^2 \sin\theta\, dr\, d\theta\, d\phi = \frac{1}{(2\pi)^{3/2}} \frac{1}{4\pi\varepsilon_0} \int_0^{2\pi} d\phi \int_0^{\infty} dr\, r e^{-\lambda r} \int_0^{\pi} d\theta\, e^{-ikr\cos\theta} \sin\theta$$

The integral over $\phi$ is trivial: it just gives a factor of $2\pi$.

Note that the factor $e^{-ikr\cos_\theta}$ involves $r$ and $\theta$. We should now decide which integral we do next. The presence of the $\sin\theta$ together with the $e^{-ikr\cos_\theta}$ makes integration by substitution over $\theta$ the obvious choice:

i.e. let $u = ikr\cos\theta$ so $du = -ikr\sin\theta\, d\theta$ Rewrite $\int \sin\theta\, e^{-ikr\cos\theta} d\theta = \int -\sin\theta\, e^{-u} \dfrac{du}{ikr\sin\theta} = \dfrac{e^{-u}}{ikr}$

$$\text{So} \qquad \int_0^{\pi} \sin\theta e^{-ikr\cos\theta} d\theta = \frac{1}{ikr}\left[e^{-ikr\cos\theta}\right]_0^{\pi} = \frac{1}{ikr}\left(e^{ikr} - e^{-ikr}\right) = \frac{1}{kr} 2\sin kr = \frac{2\sin kr}{kr} = 2\operatorname{sinc}(kr)$$

We are then left with the integral over $r$:

$$F(k) = \frac{1}{(2\pi)^{3/2}} \frac{1}{4\pi\varepsilon_0} 2\pi \int_0^{\infty} dr\, r e^{-\lambda r} \frac{2\sin kr}{kr} \quad = \quad \frac{1}{(2\pi)^{3/2}} \frac{1}{\varepsilon_0 k} \int_0^{\infty} (\sin kr)\, e^{-\lambda r}\, dr.$$

This type of integral was met earlier in the tutorial question exercises on Fourier transforms. The trick is to write the sine in terms of complex exponentials:

$$\int_0^{\infty} (\sin kr)\, e^{-\lambda r}\, dr = \frac{1}{2i} \int_0^{\infty} \left[e^{ikr} - e^{-ikr}\right] e^{-\lambda r} dr = \frac{1}{2i} \int_0^{\infty} \left[e^{-r(\lambda - ik)} - e^{-r(\lambda + ik)}\right] dr = \frac{1}{2i}\left[\frac{1}{\lambda - ik} - \frac{1}{\lambda + ik}\right] = \frac{k}{\lambda^2 + k^2}$$

This gives the final result: $F(k) = \dfrac{1}{(2\pi)^{3/2}} \dfrac{1}{\varepsilon_0(\lambda^2 + k^2)}$ .

## The Spherical Harmonics

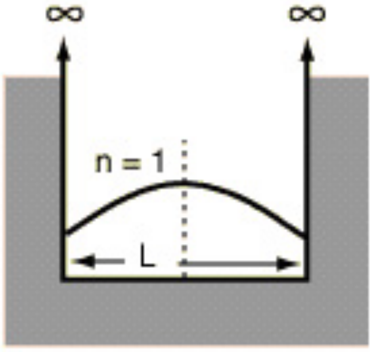
*References*: Course Pack p.83-86, 125-128.

Previously we stated that for spherical polar coordinates,

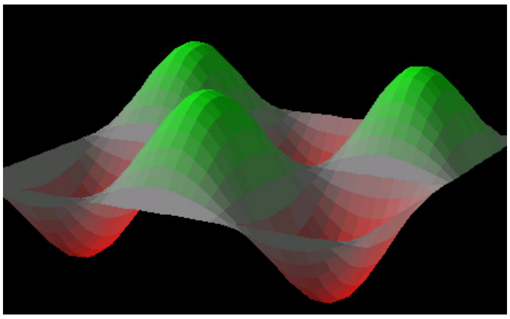
$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}.$$

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.

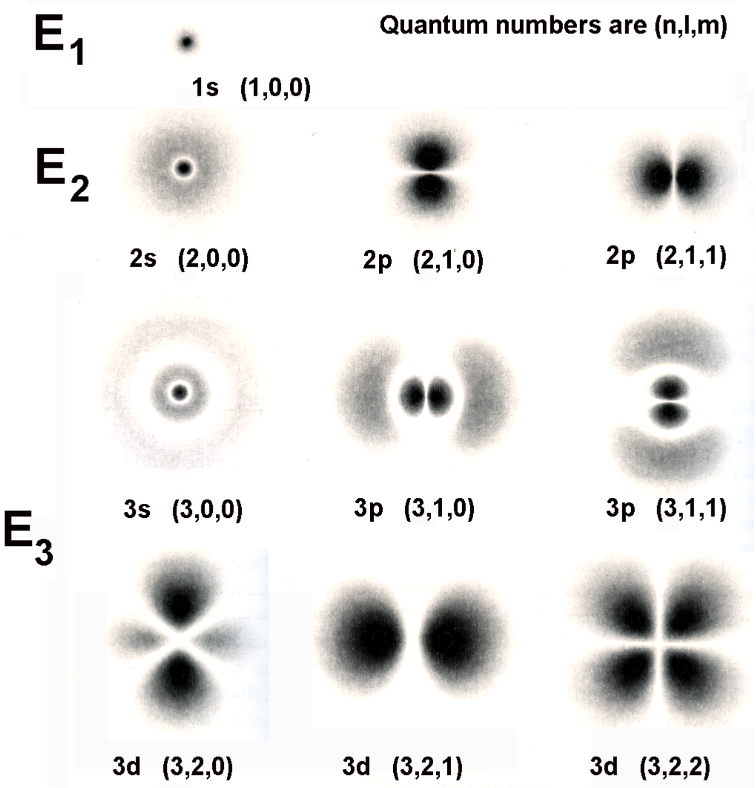
Bohr and Schrodinger both predicted that the energy levels of the H atom were: $E_n = -\frac{13.6\text{ eV}}{n^2}$.

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 3rd excited state can be in ($n$=3, $l$=0), or ($n$=3, $l$=1) or ($n$=3, $l$=2) quantum states.

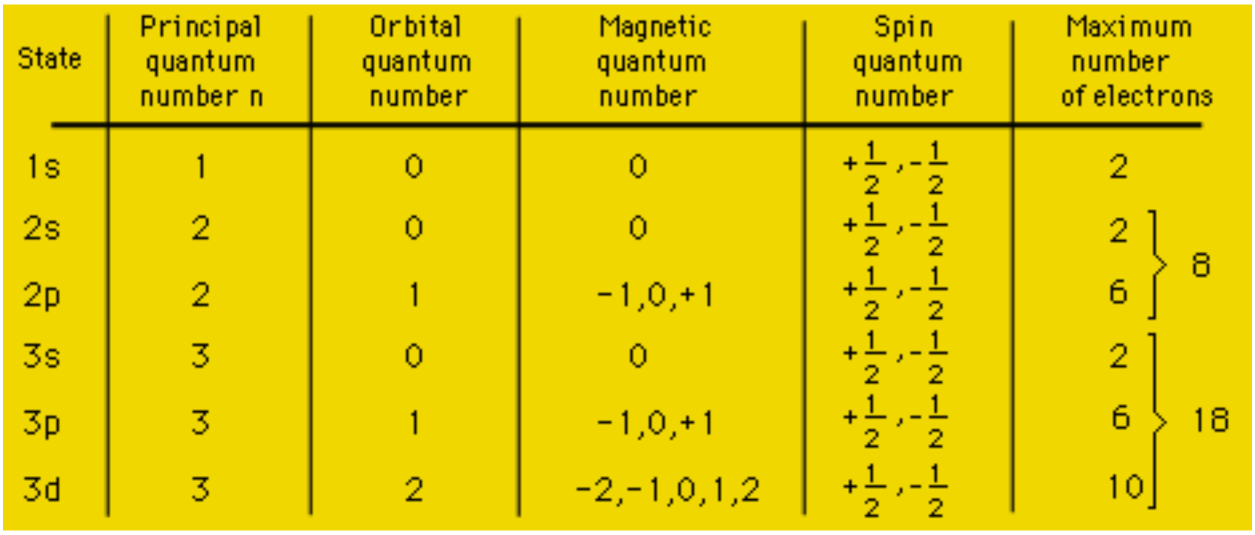
In addition each one of these quantum states has further states represented by another quantum number $m$ defined as the magnetic quantum number. Whereas $l$ is a positive integer, $m$ is a positive or negative integer where $|m| \leq l$. This means that for a given *l,* there are *2l*+1 allowed values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

(A 4th 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, 1st and 2nd 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 | 8 |
| 2p | 2 | 1 | -1,0,+1 | $+\frac{1}{2},-\frac{1}{2}$ | 6 | |
| 3s | 3 | 0 | 0 | $+\frac{1}{2},-\frac{1}{2}$ | 2 | 18 |
| 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 | | |
|---|---|---|---|---|---|
| $n$ | $l$ | $m$ | $R(r)$ | $P(\theta)$ | $F(\varphi)$ |
| 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 | ±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 | ±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 | $\frac{4}{81\sqrt{30}a_0^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}$ | $\frac{\sqrt{10}}{4}\left(3\cos^2\theta-1\right)$ | $\frac{1}{\sqrt{2\pi}}$ |

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.

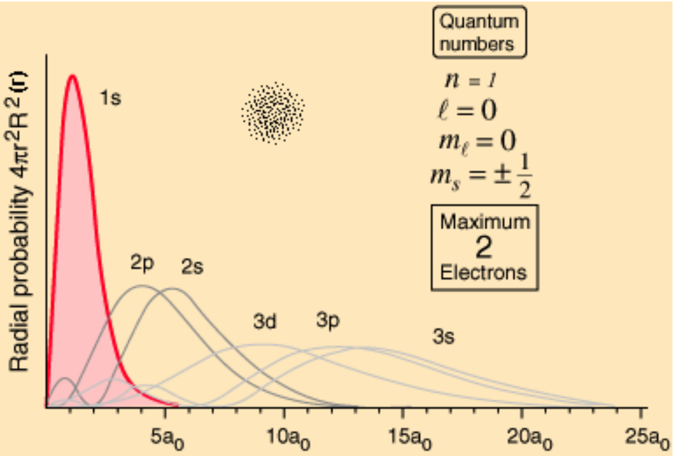
For the (1,0,0) harmonic mode

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

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

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

It takes this comparatively simple form because the 1$s$ 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.



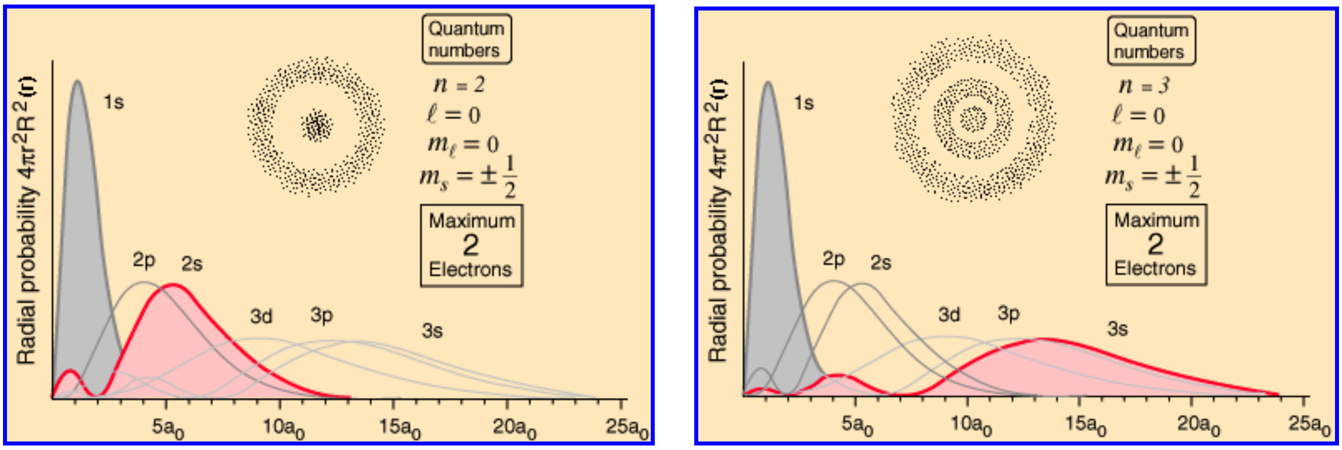
$$dP = \frac{1}{\pi a_0^3} e^{-2r/a_0} 4\pi r^2 dr$$

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

$$P = \int_0^\infty \frac{1}{\pi a_0^3} e^{-2r/a_0} 4\pi r^2 dr = \int_0^\infty \frac{4r^2}{a_0^3} e^{-2r/a_0} dr = \frac{4}{a_0^3}\left[e^{-2r/a_0}\left(\frac{-a_0 r^2}{2} - \frac{a_0^2 r}{2} - \frac{a_0^3}{4}\right)\right]_0^\infty = 1.$$

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* states) would be a function of $\theta$ and $\varphi$ 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.

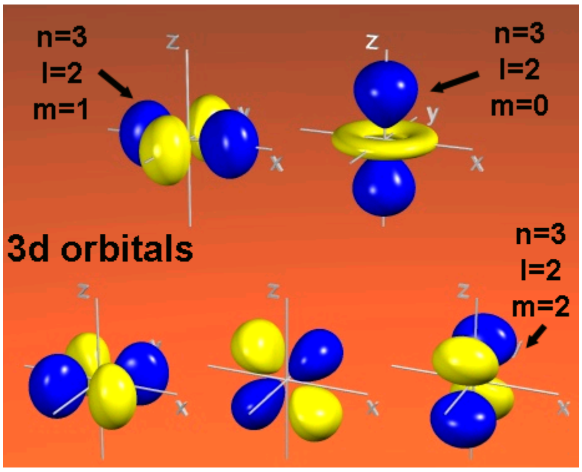


From Hyperphysics website: http://hyperphysics.phy-astr.gsu.edu/Hbase/hydwf.html#c1

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 3*d* 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 $m$: $m = 0, \pm 1, \pm 2, .. \pm l$. 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 $\varphi$ 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. In spherical harmonics $l$ 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 before, the Laplace equation in spherical polar coordinates is written:

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

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

Substituting this into the PDE gives:

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

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

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

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

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

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

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

And we need periodicity of $2\pi$, i.e. we need $\sin(m\phi) = \sin(m\phi + 2m\pi)$, 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 next 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 | $Y_1^{\pm1}(\theta,\phi)=\mp\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{\pm i\phi}$ |  |
| 2 | 0 | $Y_2^0(\theta,\phi)=\sqrt{\frac{5}{16\pi}}\left(3\cos^2\theta-1\right)$ | $d$ |
|  | ±1 | $Y_2^{\pm1}(\theta,\phi)=\mp\sqrt{\frac{5}{24\pi}}3\sin\theta\cos\theta\, e^{\pm i\phi}$ |  |
|  | ±2 | $Y_2^{\pm1}(\theta,\phi)=\mp\sqrt{\frac{5}{96\pi}}3\sin^2\theta\, e^{\pm2i\phi}$ |  |
| 3 | 0 | $Y_3^0(\theta,\phi)=\sqrt{\frac{7}{16\pi}}\left(5\cos^3\theta-3\cos\theta\right)$ | $f$ |
|  | ±1 | $Y_3^{\pm1}(\theta,\phi)=\mp\sqrt{\frac{21}{64\pi}}\sin\theta\left(5\cos^2\theta-1\right) e^{\pm i\phi}$ |  |
|  | ±2 | $Y_3^{\pm2}(\theta,\phi)=\mp\sqrt{\frac{105}{32\pi}}\sin^2\theta\cos^2\theta\, e^{\pm2i\phi}$ |  |
|  | ±3 | $Y_3^{\pm3}(\theta,\phi)=\mp\sqrt{\frac{35}{64\pi}}\sin^3\theta\, e^{\pm3i\phi}$ |  |