6 Wave equation in spherical polar coordinates

We now look at solving problems involving the Laplacian in spherical polar coordinates. The angular dependence of the solutions will be described by *spherical harmonics*.
We take the wave equation as a special case:

$$\nabla^2 u = \frac{1}{c^2}\frac{\partial^2 u}{\partial t^2}$$

The Laplacian given by Eqn. (4.11) can be rewritten as:

$$\nabla^2 u = \underbrace{\frac{\partial^2 u}{\partial r^2} + \frac{2}{r}\frac{\partial u}{\partial r}}_{\text{radial part}} + \underbrace{\frac{1}{r^2 \sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial u}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2 u}{\partial\phi^2}}_{\text{angular part}} . \tag{6.1}$$

6.1 Separating the variables

We consider solutions of separated form

$$u(r,\theta,\phi,t) = R(r)\ \Theta(\theta)\ \Phi(\phi)\ T(t) .$$

Substitute this into the wave equation and divide across by $u = R\Theta\Phi T$:

$$\frac{1}{R}\frac{d^2R}{dr^2} + \frac{2}{rR}\frac{dR}{dr} + \frac{1}{r^2}\frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = \frac{1}{c^2}\frac{1}{T}\frac{d^2T}{dt^2}.$$

6.1.1 First separation: r, θ, ϕ versus t

$$\text{LHS}(r,\theta,\phi) = \text{RHS}(t) = \text{constant} = -k^2.$$

This gives the T equation:

$$\frac{1}{c^2}\frac{1}{T}\frac{d^2T}{dt^2} = -k^2 \tag{6.2}$$

which is easy to solve.

6.1.2 Second separation: θ, ϕ versus r

Multiply LHS equation by r^2 and rearrange:

$$-\frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) - \frac{1}{\sin^2\theta}\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = \frac{r^2}{R}\frac{d^2R}{dr^2} + \frac{2r}{R}\frac{dR}{dr} + k^2r^2 . \tag{6.3}$$

$$\text{LHS}(\theta,\phi) = \text{RHS}(r) = \text{constant} = \lambda$$

We choose the separation constant to be λ. For later convenience, it will turn out that $\lambda = l(l+1)$ where l has to be integer.
Multiplying the RHS equation by R/r^2 gives the R equation:

$$\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr} + \left[k^2 - \frac{\lambda}{r^2}\right]R = 0. \tag{6.4}$$

This can be turned into Bessel's equation; we'll do this later.

6.1.3 Third separation: θ versus ϕ

Multiply LHS of Eqn. (6.3) by $\sin^2\theta$ and rearrange:

$$\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \lambda\sin^2\theta = -\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = m^2$$

$$\mathrm{LHS}(\theta) = \mathrm{RHS}(\phi) = \text{constant} = -m^2 \ .$$

The RHS equation gives the Φ equation without rearrangement:

$$\frac{d^2\Phi}{d\phi^2} = -m^2\Phi \ . \qquad (6.5)$$

Multiply the LHS by $\Theta/\sin^2\theta$ to get the Θ equation:

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \left[\lambda - \frac{m^2}{\sin^2\theta}\right]\Theta = 0 \ . \qquad (6.6)$$

6.2 Solving the separated equations

Now we need to solve the ODEs that we got from the original PDE by separating variables.

6.2.1 Solving the T equation

Eqn. (6.2) is of simple harmonic form and solved as before, giving sinusoids as solutions:

$$\frac{d^2T}{dt^2} = -c^2k^2T \equiv -\omega_k^2 T \ ,$$

with $\omega_k = ck$.

6.2.2 Solving the Φ equation

Eqn. (6.5) is easily solved. Rather than using cos and sin, it is more convenient to use complex exponentials:

$$\Phi(\phi) = e^{\pm im\phi}$$

Note that we have to include both positive and negative values of m.
As ϕ is an angular coordinate, we expect our solutions to be *single-valued*, i.e. unchanged as we go right round the circle $\phi \to \phi + 2\pi$:

$$\Phi(\phi + 2\pi) = \Phi(\phi) \qquad \Rightarrow \qquad e^{i2\pi m} = 1 \qquad \Rightarrow \qquad m = \text{integer}.$$

This is another example of a BC (periodic in this case) quantising a separation constant.
In principle m can take any integer value between $-\infty$ and ∞.
It turns out in Quantum Mechanics that

m is the integer magnetic quantum number and $-l \le m \le l$

for the z-component of angular momentum. In that context we will see that it is restricted to the range $-l \le m \le l$.

6.2.3 Solving the Θ equation

Starting from Eqn. (6.6), make a change of variables $w = \cos\theta$:

$$\begin{aligned}
\frac{d}{dw} &= \frac{d\theta}{dw}\frac{d}{d\theta} = \left(\frac{dw}{d\theta}\right)^{-1}\frac{d}{d\theta} = -\frac{1}{\sin\theta}\frac{d}{d\theta} \,, \\
(1-w^2)\frac{d}{dw} &= -\frac{1-\cos^2\theta}{\sin\theta}\frac{d}{d\theta} = -\frac{\sin^2\theta}{\sin\theta}\frac{d}{d\theta} = -\sin\theta\frac{d}{d\theta} \,, \\
\frac{d}{dw}(1-w^2)\frac{d}{dw} &= -\frac{1}{\sin\theta}\frac{d}{d\theta}\left[-\sin\theta\frac{d}{d\theta}\right] = \frac{1}{\sin\theta}\frac{d}{d\theta}\left[\sin\theta\frac{d}{d\theta}\right] \,.
\end{aligned}$$

Eqn. (6.6) becomes

$$\left(\frac{d}{dw}(1-w^2)\frac{d}{dw} + \lambda - \frac{m^2}{1-w^2}\right)\Theta(w) = 0 \,.$$

which is known as the *Associated Legendre Equation*. Solutions of the Associated Legendre Equation are the Associated Legendre Polynomials. Note that the equation depends on m^2 and the equation and solutions are the same for $+m$ and $-m$.

It will turn out that there are smart ways to generate solutions for $m \neq 0$ from the solutions for $m = 0$ using angular momentum ladder operators (see quantum mechanics of hydrogen atom). So it would be unnecessarily “heroic” to directly solve this equation for $m \neq 0$.

In this course we will only solve this equation for $m = 0$.

6.2.4 Solving the Legendre equation

For $m = 0$ we can write the special case as the *Legendre Equation*:

$$\left((1-w^2)\frac{d^2}{dw^2} - 2w\frac{d}{dw} + \lambda\right)\Theta(w) = 0 \,.$$

We apply the method of Froebenius by taking

$$\Theta(w) = \sum_{i=0}^{\infty} c_i w^i$$

Then

$$\sum_{i=0}^{\infty} c_i i(i-1)(w^{i-2} - w^i) - 2c_i i w^i + \lambda c_i w^i = 0$$

and rearranging the series to always refer the power w^i,

$$\sum_{i=0}^{\infty} \left[c_{i+2}(i+2)(i+1) + c_i(\lambda - i(i-1) - 2i\right] w^i = 0$$

Since this is true for all w, it is true term by term, and the indicial equation is

$$\boxed{c_{i+2}\left((i+2)(i+1)\right) = c_i\left(i(i+1) - \lambda\right)}$$

Start The series ”switches on” when $c_0 \times 0 = 0$ admits $c_0 \neq 0$ and $c_{-2} = 0$
Also when $c_1 \times 0 = 0$ admits $c_1 \neq 0$ and $c_{-1} = 0$.

Termination Note, however $c_{i+2} \simeq c_i$ for large i. This gives an ill convergent series and for finite solutions the series must terminate at some value of i, which we call l. Thus,

$$\lambda = l(l+1)$$

for some (quantised) integer value l.

It will turn out in quantum mechanics that l is the orbital angular momentum quantum number.

6.2.5 Legendre polynomials

We denote the solutions the Legendre polynomials

$$P_l(w) \equiv P_l(\cos\theta)$$

For example: P_0 starts, and terminates with a single term C_0.
P_1 starts, and terminates with a single term C_1.
P_2 starts, with C_0 and terminates on C_2.
etc...
The first few are

$$\begin{aligned} P_0(w) &= 1 \\ P_1(w) &= w \\ P_2(w) &= \frac{1}{2}(3w^2-1) \\ P_3(w) &= \frac{1}{2}(5w^3-3w) \end{aligned}$$

Exercise: use the recurrence relation

$$c_{i+2}\left((i+2)(i+1)\right) = c_i\left(i(i+1) - l(l+1)\right)$$

to verify that these are our series solutions of Legendre's equation.

6.2.6 Orgthogonality

The orthogonality relation is

$$\int_{-1}^{1} P_m(w)P_n(w)dw = \int_0^\pi P_m(\cos\theta)P_n(\cos\theta)\sin\theta d\theta = N_m\delta_{mn}$$

where N_m is a normalisation factor that we do not need here.
In quantum mechanics this is already sufficient to cover S, P , D and F orbitals.

6.2.7 Associated Legendre polynomials

As mentioned the associated Legendre polynomials can be produced from Legendre polynomials in quantum mechanics using angular momentum ladder operators. Firstly,

$$P_l^0(w) = P_l(w)$$

Without proof, we can note that it can be shown that if $P_l(w)$ satisfies Legendre's equation, then

$$P_l^{|m|}(w) = (1-w^2)^{|m|/2} \frac{d^{|m|}}{dw^{|m|}} P_l(w)$$

will satisfy the associated Legendre polynomial for magnetic quantum number m.
As P_l is a polynomial of order l, then the above m-th derivative vanishes for $|m| > l$ and thus $m = -l, -l+1, \ldots, 0, \ldots l-1, l$.

6.2.8 General angular solution

Putting aside the radial part for the moment, the rest of the general solution is:

$$\Theta(\theta)\Phi(\phi)T(t) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} P_l^m(\cos\theta)\, e^{im\phi}\ \ (E_{ml}\cos\omega_k t + F_{ml}\sin\omega_k t)$$

The angular dependence is given by the combination:

$$P_l^m(\cos\theta)\, e^{im\phi} \propto Y_m^l(\theta,\phi)$$

These are known as the *spherical harmonics* (once we include a normalisation constant). We'll discuss these more in Sec. 6.3. What we have not yet established is the link between the value of k (and hence ω_k) and the values of m and l. To do this, we would need to solve the radial equation for various special cases.

6.3 The spherical harmonics

Spherical harmonics $\{Y_l^m(\theta,\phi)\}$ provide a complete, orthonormal basis for expanding the angular dependence of a function. They crop up a lot in physics because they are the normal mode solutions to the angular part of the Laplacian. They are defined as:

$$Y_l^m(\theta,\phi) = \frac{(-1)^m}{\sqrt{2\pi}} \sqrt{\frac{2l+1}{2} \cdot \frac{(l-m)!}{(l+m)!}} P_l^m(\cos\theta) e^{im\phi} \ .$$

The extra factor of $(-1)^m$ introduced is just a convention and does not affect the orthonormality of the functions.
The spherical harmonics satisfy an orthogonality relation:

$$\int_0^{2\pi} d\phi \int_0^{\pi} d\theta\ \sin\theta\ \left[Y_{l_1}^{m_1}(\theta,\phi)\right]^* Y_{l_2}^{m_2}(\theta,\phi) = \delta_{l_1,l_2}\delta_{m_1,m_2} \ .$$

Note that they are orthonormal, not just orthogonal, as the constant multiplying the product of Kronecker deltas is unity.

6.3.1 Completeness and the Laplace expansion

The completeness property means that any function $f(\theta,\phi)$ evaluated over the surface of the unit sphere can be expanded in the double series known as the *Laplace series*:

$$f(\theta,\phi) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} a_{lm} Y_l^m(\theta,\phi) \ ,$$

$$\Rightarrow \qquad a_{lm} = \int_0^{\pi} d\theta \int_{-\pi}^{\pi} d\phi\ \sin\theta\ [Y_l^m(\theta,\phi)]^* f(\theta,\phi) \ .$$

Note that the sum over m only runs from $-l$ to l, because the associated Laplace polynomials P_l^m are zero outside this range.

6.4 Time independent Schroedinger equation in central potential

Consider

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\boldsymbol{x}) + \tilde{V}(r)\psi(\boldsymbol{x}) = \tilde{E}\psi(\boldsymbol{x}).$$

We consider solutions of separated form: $\psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi)$. Substitute into Schroedinger equation and divide across by $\psi = R\Theta\Phi$.

$$\frac{2m}{\hbar^2}(V(r)-E) - \frac{1}{R}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}R = \frac{1}{\Theta}\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\Theta + \frac{1}{\Phi}\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\Phi$$

Multiplying through by r^2

$$r^2\frac{2m}{\hbar^2}(V(r)-E) - \frac{1}{R}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}R = \frac{1}{\Theta}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\Theta + \frac{1}{\Phi}\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\Phi$$

First separation: radial & angular dependence

$$\text{LHS}(r) = \text{RHS}(\theta,\phi) = \text{constant} = -l(l+1).$$

6.4.1 Radial equation

$$\left[-\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + l(l+1) + r^2\frac{2m}{\hbar^2}(V(r)-E)\right]R = 0$$

The differential equation is simplified by a substitution,

$$\begin{aligned} u(r) &= rR(r) \\ u'(r) &= R(r) + rR'(r) \\ u''(r) &= 2R'(r) + rR''(r) = \frac{1}{r}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}R \end{aligned}$$

and so

$$\left[-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + \frac{2m}{\hbar^2}(V(r)-E)\right]u(r) = 0$$

We take a Coulomb potential and will be considering bound states, with $E<0$. It is convenient to rewrite in terms of the modulus $|E|$ and introduce explicit negative sign. We also change variables to $\rho = \frac{\sqrt{8m|E|}}{\hbar}r$

$$V(r) = \frac{-e^2}{4\pi\epsilon_0 r} = \frac{-e^2\sqrt{8m|E|}}{4\pi\epsilon_0\hbar\rho},$$

and so multiplying by $\frac{1}{r}$ and expressing in terms of u

$$\left\{\frac{8m|E|}{\hbar^2}\left[-\frac{d^2}{d\rho^2} + \frac{l(l+1)}{\rho^2}\right] + \frac{2m}{\hbar^2}\left[|E| - \frac{e^2}{4\pi\epsilon_0\rho}\sqrt{\frac{8m|E|}{\hbar^2}}\right]\right\}u(\rho) = 0$$

We define $\lambda = \frac{e^2}{4\pi\epsilon_0\hbar}\sqrt{\frac{m}{2|E|}} = \alpha\sqrt{\frac{mc^2}{2|E|}}$, where $\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} \simeq \frac{1}{137}$ is the fine structure constant. This gives us

$$\left[\frac{d^2}{d\rho^2} - \frac{1}{4} - \frac{l(l+1)}{\rho^2} + \frac{\lambda}{\rho}\right]u(\rho) = 0$$

6.4.2 Solution by method of Froebenius

We are now (almost!) ready to apply the method of Froebenius. In principle it could immediately be applied and we would get a an infinite Taylor series that indeed solves the equation.
However, a closed form solution can be obtained with one extra transformation that removes an over all exponential dependence on ρ. Observe that this equation for large ρ tends to

$$\rightarrow \left[\frac{d^2}{d\rho^2} - \frac{1}{4}\right] u(\rho)$$

which has as a normalisable solution $u(\rho) \rightarrow e^{-\frac{\rho}{2}}$ (and in addition a non-normalisable solution $u(\rho) \rightarrow e^{+\frac{\rho}{2}}$ which we ignore).
We can do rather better by taking a trial solution:

$$u(\rho) = e^{-\frac{\rho}{2}} f(\rho).$$

Then,

$$u' = e^{-\frac{\rho}{2}} \left[f'(\rho) - \frac{1}{2} f(\rho)\right].$$

$$u'' = e^{-\frac{\rho}{2}} \left[f''(\rho) - f'(\rho) + \frac{1}{4} f(\rho)\right].$$

Now,

$$\left[\frac{d^2}{d\rho^2} - \frac{d}{d\rho} + \cancel{\frac{1}{4}} - \cancel{\frac{1}{4}} - \frac{l(l+1)}{\rho^2} + \frac{\lambda}{\rho}\right] f(\rho) = 0$$

We now apply the method of Froebenius for a series substituting $f(\rho) = \sum_{i=0}^{\infty} c_i \rho^i$,

$$\sum_{i=0}^{\infty} c_i(i)(i-1)\rho^{i-2} - c_i(i)\rho^{i-1} - l(l+1)c_i\rho^{i-2} + \lambda c_i \rho^{i-1}$$

Thus, reexpressing so that all terms are of equal power ρ^{i-1}

$$\sum_{i=-1}^{\infty} c_{i+1}(i+1)(i)\rho^{i-1} - c_i(i)\rho^{i-1} - l(l+1)c_{i+1}\rho^{i-1} + \lambda c_i \rho^{i-1}$$

and we have the indicial equation,

$$\boxed{c_{i+1}\left[i(i+1) - l(l+1)\right] = c_i\left[i - \lambda\right]}$$

Series start: The series “switches on” for $c_k \equiv c_{i+1}$ when $i(i+1) = (k-1)k = l(l+1)$.

The first term c_k has $k = l+1$.

Series termination: If the series does not terminate, then $c_{i+1} \rightarrow \frac{c_i}{i}$, and $f \rightarrow \sum \frac{\rho^i}{i!}$. This looks like the other solution that is a non-normalisable exponential $u(\rho) \simeq e^{+\frac{\rho}{2}}$ which we do not seek.
Only if $\lambda = i = n$ then the series ”switches off” after $n - l$ terms.

$$c_{i+1} = c_i \frac{i - \lambda}{i(i+1) - l(l+1)}$$

We call n the principal quantum number. Note that for any given l, then $n \geq l+1$ as the series commences at $k = l+1$. The energy is

$$\alpha\sqrt{\frac{mc^2}{2|E|}} = n$$

Thus

$$|E| = \frac{\alpha^2 mc^2}{2n^2}$$

This energy is consistent with the Hydrogen spectrum (Lymann, Balmer series etc...).

6.4.3 Wavefunctions

We denote the radial solution for $L = l$, and principle quantum number $n \geq l+1$ as R_{nl}.
Using our recurrence relation

$$c_{i+1} = c_i \frac{i-n}{i(i+1) - l(l+1)}$$

we have

	$n=1, l=0$	$n=2, l=0$	$n=2, l=1$
c_0	0	0	0
c_1	1	1	0
c_2	0	$-\frac{1}{2}$	1
c_3	0	0	0

The above energy relation gives us that for each n

$$\begin{aligned} \rho &= \frac{\sqrt{8m|E|}}{\hbar} r && (6.7) \\ &= \frac{2}{n}\frac{\alpha mc}{\hbar} r && (6.8) \\ &= \frac{2}{n}\frac{r}{a_0} && (6.9) \end{aligned}$$

where $a_0 = \frac{\hbar}{\alpha mc}$ is the usual Bohr radius.
The solutions are then

$$\begin{aligned} R_{1S} &\propto \frac{1}{\rho} e^{-\frac{\rho}{2}} \rho && (6.10) \\ &= e^{-\frac{\rho}{2}} && (6.11) \\ &= e^{-\frac{r}{a_0}} && (6.12) \\ R_{2S} &\propto \frac{1}{\rho} e^{-\frac{\rho}{2}} \left(\rho - \frac{1}{2}\rho^2\right) && (6.13) \\ &= e^{-\frac{\rho}{2}} \left(1 - \frac{1}{2}\rho\right) && (6.14) \\ &= e^{-\frac{r}{2a_0}} \left(1 - \frac{1}{2}\frac{r}{a_0}\right) && (6.15) \\ R_{2P} &\propto \frac{1}{\rho} e^{-\frac{\rho}{2}} \rho^2 && (6.16) \\ &= e^{-\frac{\rho}{2}} \rho && (6.17) \\ &= e^{-\frac{r}{2a_0}} \frac{r}{a_0} && (6.18) \end{aligned}$$

Note, we have not carefully normalised these radial wavefunctions. For each l the different wavefunctions for the various $n > l$ are orthogonal to each other. The orthogonality relation contains a residual r^2 factor corresponding to a vestige of the required orthogonality of wavefunctions under the 3d volume integral.

$$\int_0^\infty R_{nl}(r)R_{ml}(r)r^2 dr = N_n N_m \delta_{nm}$$

A complete orthonormal set can of course be formed as usual but is beyond the scope of the course.

This concludes the examinable material of the course