

11)

THE LAPLACE OPERATOR AND THE SCHRÖDINGER EQUATION

- Laplace operator in Cartesian coordinates

Let us consider the wave equation with the ansatz $\Psi(\underline{r}, t) = e^{i\omega t} \Psi(\underline{r})$

$$\nabla^2 \Psi - \frac{1}{c^2} \frac{\partial^2 \Psi}{\partial t^2} = 0 \quad \Rightarrow \quad \nabla^2 \Psi + k^2 \Psi = 0 \quad k^2 = \frac{\omega^2}{c^2} = \text{constant}$$

↳ Helmholtz equation

We make the ansatz $\Psi(\underline{r}) = X(x) Y(y) Z(z)$

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} + k^2 \Psi = X'' Y Z + X Y'' Z + X Y Z'' + k^2 X Y Z = 0$$

$$\Rightarrow \frac{X''}{X} + \frac{Y''}{Y} + \frac{Z''}{Z} = -k^2$$

$$\frac{X''}{X} = - \underbrace{\frac{Y''}{Y} + \frac{Z''}{Z} + k^2}_{\text{independent on } X} = -e^2 \quad \text{the sign here is just for convention!}$$

Analogously we can write

$$\frac{Y''}{Y} = -m^2 \quad \frac{Z''}{Z} = -n^2 \quad e^2 + m^2 + n^2 = k^2$$

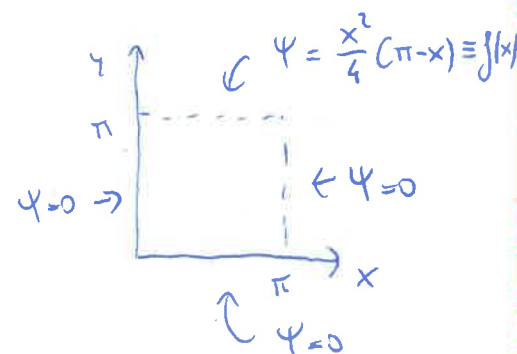
⇒ Separation of variables: a partial differential equation becomes equivalent to three ordinary diff. eqs.

EXAMPLE

We search for a solution of $\nabla^2 \Psi = 0$ in 2 dimensions

with Dirichlet boundary conditions

$$\Psi(x, y) = X(x) Y(y) \quad \Rightarrow \quad \begin{aligned} X'' &= -e^2 X \\ Y'' &= e^2 Y \end{aligned}$$



Given the boundary conditions \Rightarrow choose $e^2 > 0$!

$$X_c(x) = a x_c \sin ex + b x_c \cos ex$$

$$Y_c(y) = a_y e^{ly} + b_y e^{-ly}$$

$$\Rightarrow \text{the general solution is } \Psi(x,y) = \sum_e (k_{e1} \sin ex e^{ly} + k_{e2} \cos ex e^{ly} + k_{e3} \sin ex e^{-ly} + k_{e4} \cos ex e^{-ly})$$

Note that at this step e is arbitrary

\Rightarrow the sum over e should be an integral!

We now impose the boundary conditions:

$$- \Psi(0,y) = 0 \Rightarrow \sum_e (k_{e2} e^{ly} + k_{e4} e^{-ly}) = 0 \quad \forall y \Rightarrow k_{e2} = k_{e4} = 0$$

$$- \Psi(x,0) = 0 \Rightarrow \sum_e (k_{e1} \sin ex + k_{e3} \sin ex) = 0 \quad \forall x \Rightarrow k_{e1} = -k_{e3}$$

$$- \Psi(\pi,y) = 0 \Rightarrow \sum_e k_{e1} (e^{ly} \sin e\pi - e^{-ly} \sin e\pi) = 0 \Rightarrow \text{It must vanish } \forall y \Rightarrow e \in \mathbb{Z}$$

\Rightarrow we can limit the summation to integers! (we can restrict to $e > 0$ because e is arbitrary)

$$\Psi(x,\pi) = \sum_{e \in \mathbb{N}} 2k_{e1} \sin ex \sinh e\pi = f(x)$$

To exploit this condition, let us extend $f(x) \rightarrow \bar{f}(x)$ such that $\bar{f}(x) = \begin{cases} \frac{x^2}{4} (\pi-x) & x > 0 \\ -\frac{x^2}{4} (\pi+x) & x < 0 \end{cases}$



$$\bar{f}(x) = \sum_{n=1}^{\infty} b_n \sin nx$$

only $\sin nx$ because the function is odd!

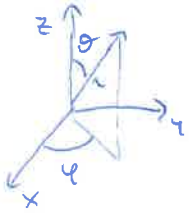
$$b_n = \frac{1}{\pi} \int_{-\pi}^{\pi} \bar{f}(x) \sin nx = -\frac{1+2(-1)^n}{n^3}$$

$$\Rightarrow \sum_{e=1}^{\infty} 2k_{e1} \sin ex \sinh e\pi = \sum_{e=1}^{\infty} b_e \sin ex$$

$$\Rightarrow 2k_{e1} = \frac{b_e}{\sinh e\pi}$$

$$\Rightarrow \Psi(x,y) = \sum_{e=1}^{\infty} \frac{-1+2(-1)^e}{e^3 \sinh e\pi} \sin ex \sinh ey$$

LAPLACIAN IN SPHERICAL COORDINATES



$$x = r \sin \theta \cos \phi$$

$$y = r \sin \theta \sin \phi$$

$$z = r \cos \theta$$

$$\tan \phi = \frac{y}{x}$$

$$\sin^2 \theta = \frac{x^2 + y^2}{x^2 + y^2 + z^2}$$

$$z^2 = x^2 + y^2 + z^2$$

We first look for an expression of the gradient

$$\frac{\partial}{\partial x} = \frac{\partial r}{\partial x} \frac{\partial}{\partial r} + \frac{\partial \theta}{\partial x} \frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial x} \frac{\partial}{\partial \phi}$$

$$= \frac{x}{r} \frac{\partial}{\partial r} + \frac{1}{r} \left(-\frac{y}{x} \right) \frac{\partial}{\partial \phi} + \frac{1}{\sqrt{x^2 + y^2}} \frac{\partial}{\partial \theta}$$

$$= \sin \theta \cos \phi \frac{\partial}{\partial r} - \frac{\sin \theta \sin \phi}{r \cos \theta} \frac{\partial}{\partial \phi} + \frac{\cos \theta \cos \phi}{r} \frac{\partial}{\partial \theta}$$

analogously

$$\frac{\partial}{\partial y} = \frac{\partial r}{\partial y} \frac{\partial}{\partial r} + \frac{\partial \theta}{\partial y} \frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial y} \frac{\partial}{\partial \phi}$$

$$\frac{\partial}{\partial z} = \frac{\partial r}{\partial z} \frac{\partial}{\partial r} + \frac{\partial \theta}{\partial z} \frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial z} \frac{\partial}{\partial \phi}$$

$$= \cos \theta \frac{\partial}{\partial r} - \frac{1}{r} \frac{\partial}{\partial \theta} = \cos \theta \frac{\partial}{\partial r} - \frac{\sin \theta}{r} \frac{\partial}{\partial \theta}$$

After some algebra we get

$$\frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial f}{\partial r} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial}{\partial \phi} \left(\sin^2 \theta \frac{\partial f}{\partial \phi} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin^2 \theta \frac{\partial f}{\partial \theta} \right)$$

we also have $\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) = \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r}$

4)

Let us now study the Laplace equation in spherical coordinates

$$\nabla^2 \psi = 0 \quad \psi = \psi(r, \theta, \varphi)$$

→ the $\frac{1}{r}$ factor is just for convention;

separation of variables $\psi(r, \theta, \varphi) = \frac{U(r)}{r} P(\theta) Q(\varphi)$ ↳ but it makes calculations simpler

$$\frac{\partial^2}{\partial r^2} \left(\frac{\psi}{r} \right) + \frac{2}{r} \frac{\partial}{\partial r} \left(\frac{\psi}{r} \right) = \frac{\partial}{\partial r} \left(\frac{\psi'}{r} - \frac{\psi}{r^2} \right) + \frac{2}{r} \left(\frac{\psi'}{r} - \frac{\psi}{r^2} \right) = \frac{\psi''}{r}$$

$$\Rightarrow \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{1}{r^2 \sin^2 \theta} \frac{\partial}{\partial \varphi} \sin \theta \frac{\partial}{\partial \varphi} + \frac{1}{r^2 \sin \theta} \frac{\partial^2}{\partial \theta^2} \right) \psi(r, \theta, \varphi) = 0$$

implies

$$P Q U'' + \frac{U Q}{r^2 \sin \theta} \frac{d}{d\theta} (\sin \theta P') + \frac{U P Q''}{r^2 \sin^2 \theta} = 0$$

$$r^2 \sin^2 \theta \frac{U''}{U} + \frac{\sin \theta}{P} \frac{d}{d\theta} (\sin \theta P') + \frac{Q''}{Q} = 0$$

independent on φ ⇒ $\frac{Q''}{Q}$ must be independent on φ $\frac{Q''}{Q} = -m^2$

$$\Rightarrow Q(\varphi) = e^{\pm i m \varphi}$$

in order for this function to have the same value at 0 and 2π we must have $m \in \mathbb{Z}$!

$$r^2 \frac{U''}{U} + \frac{1}{P \sin \theta} \frac{d}{d\theta} (\sin \theta P') - \frac{m^2}{\sin^2 \theta} = 0$$

independent on θ ⇒ $r^2 \frac{U''}{U} = \text{const} = l(l+1)$

We have now recast the PDE in two ordinary diff. equations

$$\left\{ \begin{array}{l} \frac{1}{\sin \theta} \frac{d}{d\theta} (\sin \theta P') + \left(l(l+1) - \frac{m^2}{\sin^2 \theta} \right) P = 0 \\ U'' - \frac{l(l+1)}{r^2} U = 0 \end{array} \right.$$

5) Let us focus on the first equation and let $x = \cos \theta \Rightarrow \sin^2 \theta = 1 - x^2$

$$\frac{d}{d\theta} = \frac{dx}{d\theta} \frac{d}{dx} = \sin \theta \frac{d}{dx} \Rightarrow \frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d}{d\theta} \right) = \frac{d}{dx} (1-x^2) \frac{d}{dx}$$

and the equation becomes

$$\boxed{\frac{d}{dx} (1-x^2) \frac{dP}{dx} + \left[\ell(\ell+1) - \frac{m^2}{1-x^2} \right] P = 0} \quad *$$

In the case $m=0$ this is the equation of ORDINARY LEGENDRE POLYNOMIALS

→ Rodriguitz formula

$$(1-x^2)P'' - 2xP' + \ell(\ell+1)P = 0$$

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

In the case $m \neq 0$ the solutions of the diff. equation are the associated Legendre Polynomials

$$\text{Let us set } P = (1-x^2)^{m/2} z(x)$$

$$P' = (1-x^2)^{m/2} z' - mx(1-x^2)^{m/2-1} z$$

$$P'' = (1-x^2)^{m/2} z'' + \frac{m}{2}(-2x)(1-x^2)^{m/2-1} z' - m(1-x^2)^{m/2-1} z - mx(-2x) \left(\frac{m}{2}-1\right) (1-x^2)^{m/2-2} z - mx(1-x^2)^{m/2-1} z'$$

$$= (1-x^2)^{m/2} z'' - 2mx(1-x^2)^{m/2-1} z' + m(x^2(m-1)-1)(1-x^2)^{m/2-2} z$$

$$= (1-x^2)^{m/2} z'' - 2mx(1-x^2)^{m/2-1} z' + \left(\frac{d^2}{dx^2} (1-x^2)^{m/2} \right) z$$

Replacing into the original equation and dividing by $(1-x^2)^{m/2}$ we get

$$(1-x^2) z'' - 2x(m+1) z' + [\ell(\ell+1) - m(m+1)] z = 0 \quad (1)$$

$m=0 \Rightarrow z(x) = P_\ell(x)$ is a solution

Taking the derivative we get

$$(1-x^2) z''' - 2x z'' - 2(m+1) z' - 2x(m+1) z'' + [\ell(\ell+1) - m(m+1)] z' = 0$$

setting $v = z'$

$$(1-x^2) v'' - 2(m+2)x v' + [\ell(\ell+1) - (m+1)(m+2)] v = 0 \quad (2)$$

We get (2) from (1) with $m \rightarrow m+1$ and $z \rightarrow v$

* Note that up to this point $\lambda = e(l+1)$ is an arbitrary constant

However for arbitrary values of λ the solutions of the differential equation

are DIVERGENT at $X \rightarrow \pm 1$

It is only for $\lambda = e(l+1)$, with l integer that ONE OF THE TWO SOLUTIONS is finite at $X = \pm 1$

6)

$\Rightarrow P_e(x)$ is a solution of (1) with $m=0$

$P_e'(x)$ is a solution of (1) with $m=1$

\vdots
 $P_e^{(m)}(x)$ is a solution of (1) with $m=N$

\Rightarrow the general solution of the original equation is

$$P_e^{(m)}(x) = (1-x^2)^{\frac{m}{2}} \frac{d^m}{dx^m} P_e(x)$$

\hookrightarrow vanishes for $m > e!$

Associated Legendre Polynomials

In summary: combining the solutions of the equations for θ and φ we define:

$$Y_e^{(m)}(\theta, \varphi) = \sqrt{\frac{2e+1}{4\pi} \frac{(e-m)!}{(e+m)!}} P_e^{(m)}(\cos\theta) e^{im\varphi} (-1)^m \quad m \geq 0$$

$$Y_e^{(-m)}(\theta, \varphi) = (-1)^m (Y_e^m)^*$$

SPHERICAL HARMONICS

These functions provide an orthonormal basis for the sphere with unit radius:

$$\int d\Omega \left(Y_e^{(m)} \right)^* Y_{e'}^{(m')} = \delta_{ee'} \delta_{mm'} \quad \text{basis for } L^2[S^2]$$

$$Y_0^{(0)}(\theta, \varphi) = \sqrt{\frac{1}{4\pi}}$$

$$Y_1^{(0)}(\theta, \varphi) = \sqrt{\frac{3}{4\pi}} \cos\theta$$

$$Y_1^{(\pm 1)}(\theta, \varphi) = \mp \sqrt{\frac{3}{8\pi}} \sin\theta e^{\pm i\varphi}$$

We now move to consider the radial equation

$$u'' - \frac{e(e+1)}{r^2} u = 0$$

this is an Euler equation \Rightarrow assume $u = r^d$

$$d^2 - d - e(e+1) = 0 \quad \Rightarrow \quad \begin{cases} d = e+1 \\ d = -e \end{cases}$$

\Rightarrow The general solution is $u(r) = k_1 r^{e+1} + k_2 r^{-e}$

\uparrow only this solution has regular behavior as $r \rightarrow 0$

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In studying quantum mechanics you will learn that

- r^{l+1} is relevant for bound states (regular as $r \rightarrow 0$)
- r^{-l} is relevant for scattering problems (regular as $r \rightarrow \infty$)

If we limit ourselves to solutions that are regular as $r \rightarrow 0$

we can write the general solution of $\nabla^2 \psi = 0$ as

$$\psi(r, \theta, \varphi) = \sum_{l=0}^{\infty} \sum_{m=-l}^l c_{l,m} r^l Y_l^m(\theta, \varphi)$$

7) EXAMPLE: The electric potential in an empty sphere

$$\begin{cases} \nabla^2 \psi = 0 & \text{for } r < R \\ \psi(r, \vartheta, \varphi) = f(\vartheta, \varphi) & r = R \end{cases}$$

we look for solutions of the form $\psi(r, \vartheta, \varphi) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} c_{\ell, m} r^{\ell} Y_{\ell}^m(\vartheta, \varphi)$

$$\psi(R, \vartheta, \varphi) = f(\vartheta, \varphi) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} c_{\ell, m} R^{\ell} Y_{\ell}^m(\vartheta, \varphi)$$

$$\int_0^{\pi} \sin \vartheta d\vartheta \int_0^{2\pi} d\varphi Y_{\ell}^m(\vartheta, \varphi) f(\vartheta, \varphi) = c_{\ell, m} R^{\ell}$$

LAPLACE OPERATOR IN CYLINDRICAL COORDINATES

$\nabla^2 \psi$ in cylindrical coordinates becomes $\left(\frac{\partial^2}{\partial z^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \varphi^2} + \frac{\partial^2}{\partial z^2} \right) \psi(r, \varphi, z) = 0$

$$\psi = R(r) Q(\varphi) Z(z) \Rightarrow \frac{R''}{R} + \frac{1}{r} \frac{R'}{R} + \frac{1}{r^2} \frac{Q''}{Q} + \frac{Z''}{Z} = 0$$

"kz"

$$r^2 \frac{R''}{R} + 2 \frac{R'}{R} + \frac{Q''}{Q} + r^2 k^2 = 0 \quad \Rightarrow \quad Z(z) = \alpha_k e^{kz} + \beta_k e^{-kz}$$

$$\hookrightarrow \text{constant} = -\nu^2 \quad \Rightarrow \quad Q(\varphi) = \gamma_{\nu} \sin \nu \varphi + \delta_{\nu} \cos \nu \varphi$$

ν integer to have correct behavior with φ

$$\Rightarrow r^2 R'' + r R' + (r^2 k^2 - \nu^2) R = 0 \quad \text{Bessel equation!}$$

$R = J_{\pm \nu}(kr)$ \Rightarrow but ν is integer, so we can write the general solution as

$$R(r) = J_{\nu}(kr) + m_{\nu} N_{\nu}(kr)$$

general solution

$$\psi(r, \varphi, z) = \left(J_{\nu}(kr) + m_{\nu} N_{\nu}(kr) \right) \left(\gamma_{\nu} \sin \nu \varphi + \delta_{\nu} \cos \nu \varphi \right) \left(\alpha_k e^{kz} + \beta_k e^{-kz} \right)$$

\rightarrow constants to be fixed by using boundary conditions

8) SCHRÖDINGER EQUATION

$$H = \frac{p^2}{2m} + V(x) \quad \text{Classical Hamiltonian of a particle with mass } m \text{ (energy)}$$

$$\left(p = m\underline{v} \Rightarrow \frac{p^2}{2m} = \frac{1}{2} m \underline{v}^2 \quad \text{kinetic term} \right)$$

In quantum mechanics physical observables become operators on the HS of physical states

$$\Rightarrow \underline{p} \rightarrow \hat{\underline{p}} = -i\hbar \underline{\nabla} \quad \text{with this substitution the Hamiltonian becomes an operator}$$

$$H \rightarrow \hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(\underline{x})$$

↑ Laplace operator!

$\hat{H}\psi = E\psi$ classical problem in quantum mechanics: find the eigenvalues of the Hamiltonian and the corresponding eigenfunctions ψ
 \Rightarrow stationary states

Suppose that the potential is spherically symmetric $\Rightarrow V(\underline{x}) \rightarrow V(r)$

We can use what we have learned on the Laplace operator in spherical coordinates

The equation becomes

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

Before proceeding further let us introduce the angular momentum operator:

$$\underline{L} = \underline{r} \wedge \underline{p} \rightarrow \underline{r} \wedge \hat{\underline{p}} = -i\hbar \underline{r} \wedge \underline{\nabla} \quad L_x = y p_z - z p_y$$

$$\text{If we compute } L_z = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \text{ we get} \quad L_y = z p_x - x p_z$$

$$L_z = x p_y - y p_x$$

$$L_z = -i\hbar \frac{\partial}{\partial \varphi} !$$

This means that if we go back to the solution of the Laplace equation in spherical coordinates,

$$\text{we get } L_z Q(\varphi) = -i\hbar \frac{\partial}{\partial \varphi} e^{im\varphi} = -i\hbar im e^{im\varphi} = \hbar m Q(\varphi)$$

$\Rightarrow \hbar m$ are eigenvalues of L_z !

This means that the spherical harmonics Y_{ℓ}^m correspond to angular momentum $m\hbar$

3) Let us now consider $L^2 = L_x^2 + L_y^2 + L_z^2$

By using the expression of the gradient in spherical coordinates one can show that

$$L^2 = -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\varphi^2} \right]$$

but this is exactly the expression we find in the Laplacian!

If $P_l^m(\cos\theta)$ and $Q(\varphi) = e^{im\varphi}$ are the solutions of the angular part of the

Laplace equation we have

$$\left[\frac{1}{\sin\theta} \frac{d}{d\theta} \left(\sin\theta \frac{d}{d\theta} \right) + \left(l(l+1) - \frac{m^2}{\sin^2\theta} \right) \right] P = 0 \quad \text{and} \quad m^2 = -\frac{Q''}{Q}$$

$$\Rightarrow L^2 P Q = \hbar^2 l(l+1) P Q$$

the coefficients $l(l+1)$ represent the eigenvalues of the L^2 operator!

$$\text{So we have } L^2 \Psi(r, \theta, \varphi) = \hbar^2 l(l+1) \Psi(r, \theta, \varphi) \quad \text{and} \quad L_z \Psi(r, \theta, \varphi) = \hbar m \Psi$$

$$\text{with } -l \leq m \leq l$$

The Schrödinger equation becomes

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

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

$$\Psi = \frac{u(r)}{r} Y_l^m(\theta, \varphi)$$

$$\Rightarrow u'' - \frac{1}{r^2} l(l+1) u + \frac{2m}{\hbar^2} (E - V(r)) u = 0$$

similar to what we did for $\nabla^2 \Psi = 0$

but now the radial equation is different

$$\text{Hydrogen atom } V(r) = -Ze^2/r$$

$\Rightarrow E < 0$ bound states and the solutions of the radial equation can be expressed by using Laguerre Polynomials