Spherical Harmonics

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OST FHO Campus Rapperswil

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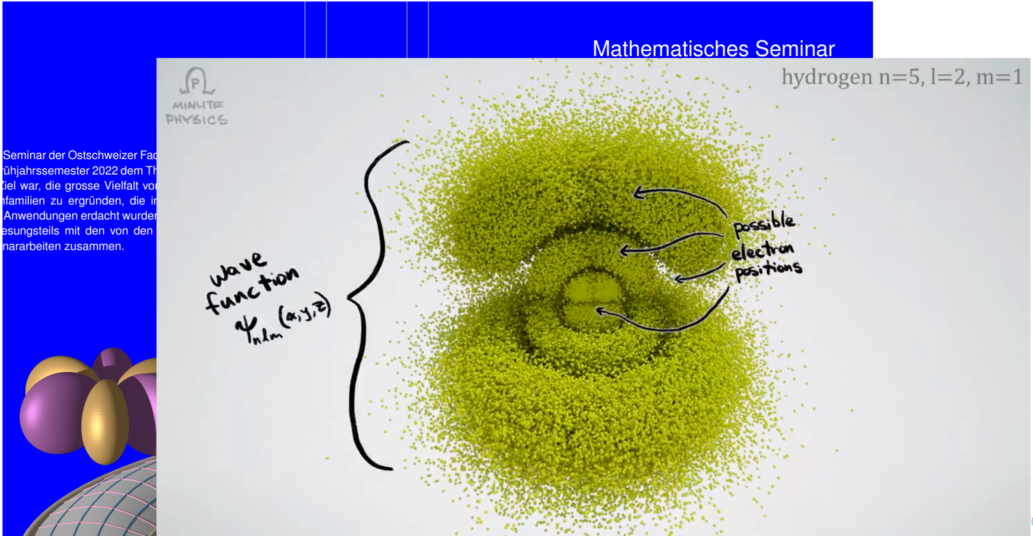
Spherical Harmonics

Goals for Today

Spherical Harmonics *and* **Electron Orbitals**



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Nice Periodic Functions

Definition

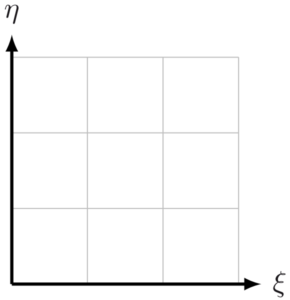
A function

$$f : \mathbb{R}^2 \to \mathbb{C}$$

is a “nice periodic function” when it is

- smooth,
- differentiable,
- (abs.) integrable,
- periodic on $[0, 1] \times [0, 1]$, i.e.

$$f(\xi, \eta) = f(\xi + 1, \eta) = f(\xi, \eta + 1).$$

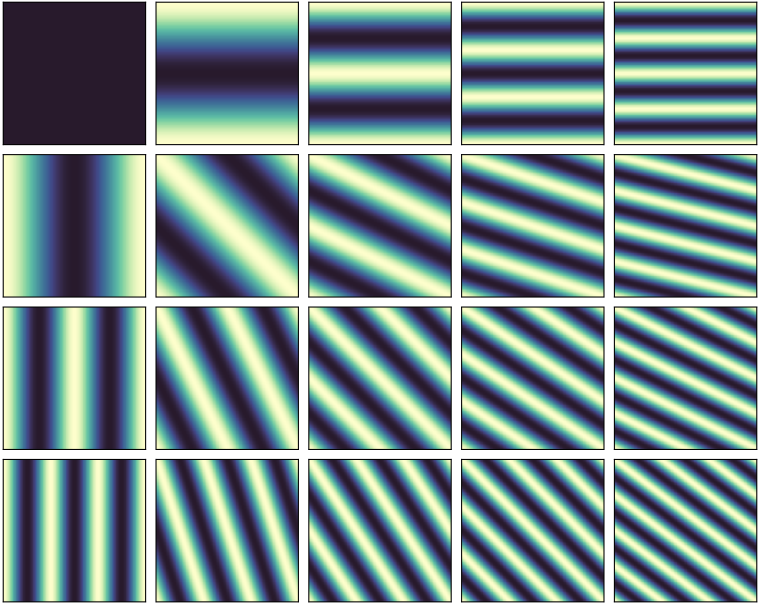


Function Space

Basis Functions

The space of nice periodic functions is spanned by the (also nice) functions

$$B_{m,n}(\xi, \eta) = e^{i2\pi m\xi} e^{i2\pi n\eta}.$$



Inner Product

Definition

Let $f(\xi, \eta)$ and $g(\xi, \eta)$ be nice periodic functions. Their inner product is

$$\langle f, g \rangle = \iint_{[0,1]^2} f(\xi, \eta)\overline{g}(\xi, \eta)\, d\xi d\eta.$$

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Definition

For a nice periodic function $f(\xi,\eta)$: the numbers

$$c_{m,n} = \langle f, B_{m,n}\rangle$$

are the *Fourier coefficients* or *spectrum* of f.

Fourier Series

Theorem

For nice periodic functions:

$$f(\xi,\eta) = \sum_{m\in\mathbb{Z}} \sum_{n\in\mathbb{Z}} c_{m,n} B_{m,n}(\xi,\eta)$$

where

$$c_{m,n} = \langle f, B_{m,n} \rangle.$$

Why exponentials?

Why $B_{m,n} = e^{i2\pi m\xi} e^{i2\pi n\eta}$ ***?***

Because ∇^2

The Problem

Fourier's Problem

$$\nabla^2 f(\xi, \eta) = \frac{\partial^2 f}{\partial \xi^2} + \frac{\partial^2 f}{\partial \eta^2} = \lambda f(\xi, \eta)$$

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$$\nabla^2 f(\xi,\eta) = \frac{\partial^2 f}{\partial \xi^2} + \frac{\partial^2 f}{\partial \eta^2} = \lambda f(\xi,\eta)$$

Solution

Separation ansatz:

$$f(\xi,\eta) = M(\xi)N(\eta)$$

Resulting ODEs:

$$\frac{d^2 M}{d\xi^2} = \kappa M(\xi), \qquad \frac{d^2 N}{d\eta^2} = (\lambda - \kappa)N(\eta)$$

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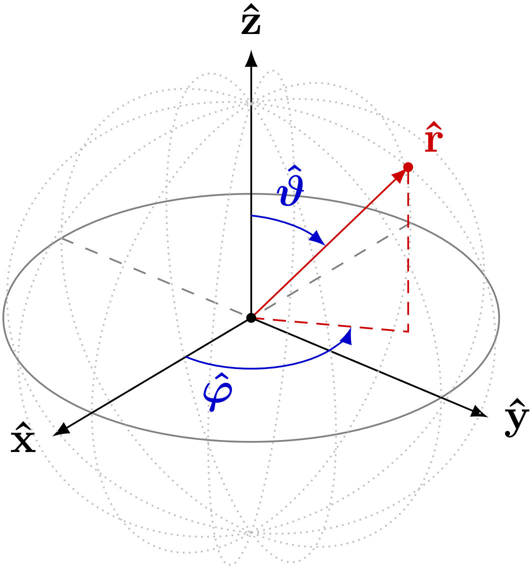
Spherical Coordinates



Variables

$$r \in \mathbb{R}^+$$
$$\vartheta \in [0, \pi]$$
$$\varphi \in [0, 2\pi)$$

To cartesian

$$x = r \cos\varphi \sin\vartheta$$
$$y = r \sin\varphi \sin\vartheta$$
$$z = r \cos\vartheta$$

Spherical Laplacian

Cartesian Laplacian

$$\nabla^2 := \frac{\partial^2}{\partial \xi^2} + \frac{\partial^2}{\partial \eta^2}$$

Spherical Laplacian

Cartesian Laplacian

$$\nabla^2 := \frac{\partial^2}{\partial \xi^2} + \frac{\partial^2}{\partial \eta^2}$$

Spherical Laplacian

$$\nabla^2 := \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2} \left[\frac{1}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \left(\sin \vartheta \frac{\partial}{\partial \vartheta} \right) + \frac{1}{\sin^2 \vartheta} \frac{\partial^2}{\partial \varphi^2} \right]$$

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Spherical Laplacian

$$\nabla^2 := \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) + \frac{1}{r^2}\underbrace{\left[\frac{1}{\sin\vartheta}\frac{\partial}{\partial \vartheta}\left(\sin\vartheta \frac{\partial}{\partial \vartheta}\right) + \frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial \varphi^2}\right]}_{\text{Surface Spherical Laplacian } \nabla_s^2}$$

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Cartesian Laplacian

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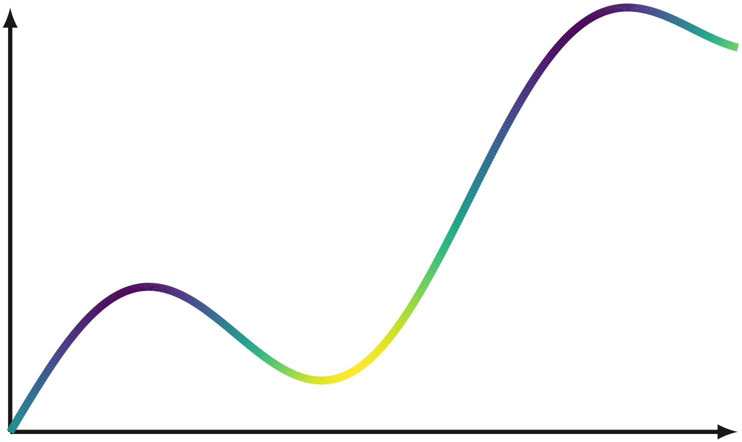
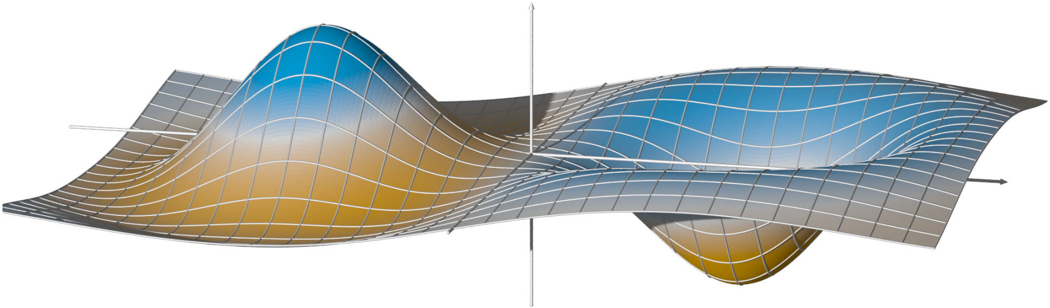
Surface Spherical Laplacian

$$\nabla_s^2 := r^2 \nabla^2 - \frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right)$$

Geometrical Intuition



Geometrical Intuition



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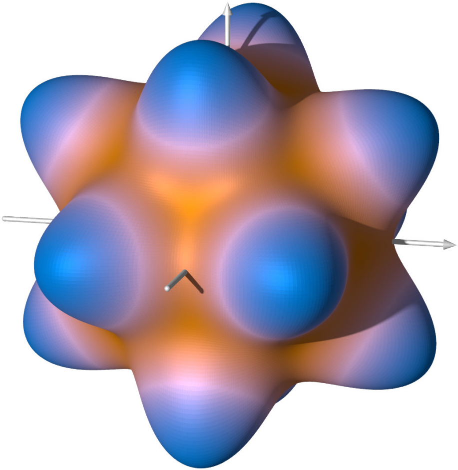
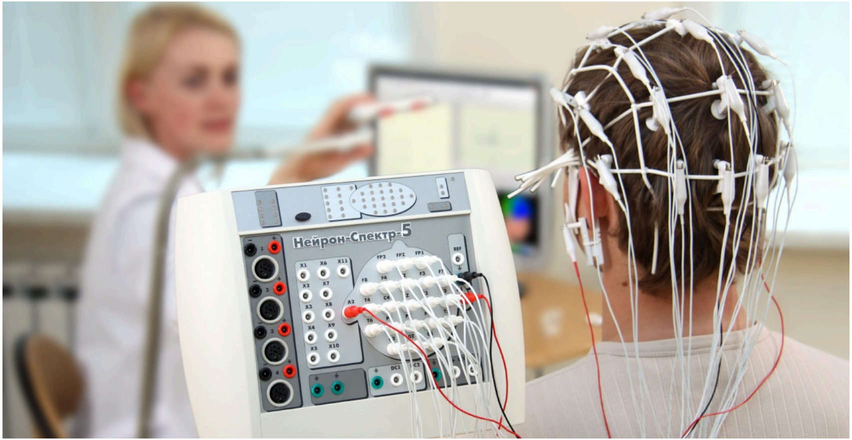


Where is ∇_s^2 useful?

To do brain scans, apparently [2]



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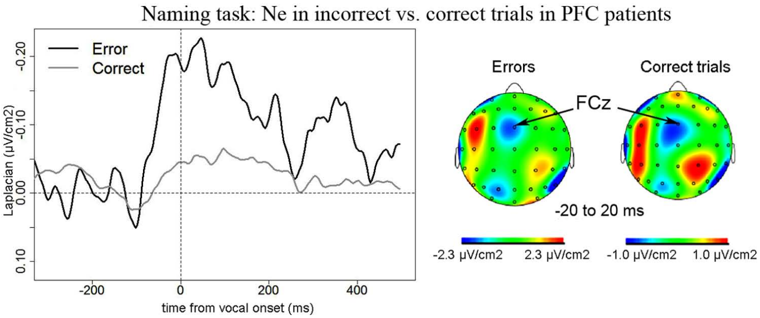

FIGURE 2 | EEG activity in PFC patients in the Naming task after surface Laplacian transformation, recorded at FCz for errors (black line) and correct trials (gray line). Zero of time represents vocal onset. The cartographies were made on a 40-ms time-window centered on vocal onset (from −20 to 20 ms after vocal onset). A 100 ms-long baseline was taken between 200 and 100 ms before vocal onset. The scale used for the topography for correct trials was larger than the one used for incorrect trials as the amplitude of the Ne was smaller in correct trials than in errors.

Brain Scans

Electrodynamics

$$\nabla^2 \phi = \boldsymbol{\nabla} \cdot \boldsymbol{\nabla} \phi \qquad \left(\phi = \int_{\mathsf{A}}^{\mathsf{B}} \mathbf{E} \cdot d\mathbf{l} \right)$$

Electrodynamics

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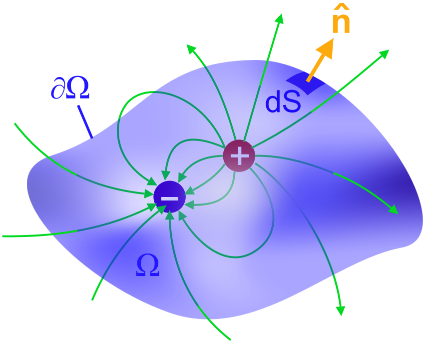
$$= \boldsymbol{\nabla}\cdot\mathbf{E}$$



Brain Scans

Electrodynamics

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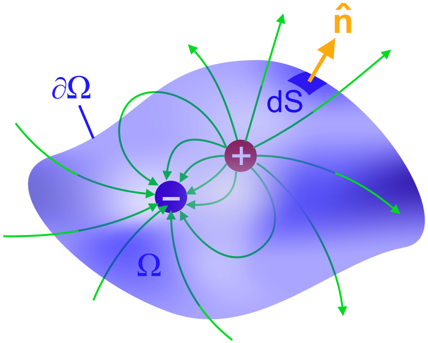
$$= \int_{\Omega} (\boldsymbol{\nabla}\cdot\mathbf{E})\cdot d\mathbf{s} = \oint_{\partial\Omega} \mathbf{E}\cdot d\mathbf{s}$$



Electrodynamics

$$\nabla^2\phi = \boldsymbol{\nabla}\cdot\boldsymbol{\nabla}\phi \qquad \left(\phi = \int_A^B \mathbf{E}\cdot dl\right)$$

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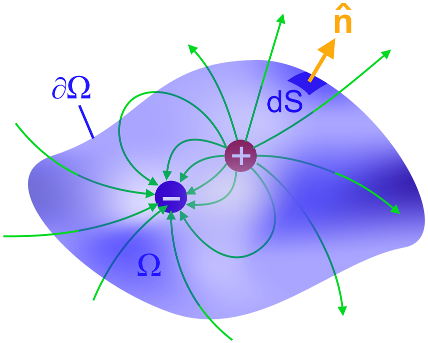
$$= \int_\Omega (\boldsymbol{\nabla}\cdot\mathbf{E})\cdot d\mathbf{s} = \oint_{\partial\Omega} \mathbf{E}\cdot d\mathbf{s}$$

$$= \frac{\rho}{\varepsilon}$$



Brain Scans

Electrodynamics

$$\nabla^2\phi = \boldsymbol{\nabla}\cdot\boldsymbol{\nabla}\phi \qquad \left(\phi = \int_{\mathsf{A}}^{\mathsf{B}} \mathbf{E}\cdot d\mathbf{l}\right)$$

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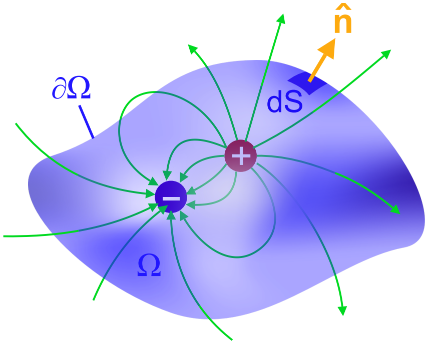

So over the scalp

$$\nabla_s^2\phi = \frac{\rho_s}{\varepsilon} = \text{Current flow in the brain}$$

New Hard Problem

The Problem

$$\nabla_s^2 f(\varphi, \vartheta) = \lambda f(\varphi, \vartheta)$$

New Hard Problem

The Problem

$$\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial f}{\partial\vartheta}\right)+\frac{1}{\sin^2\vartheta}\frac{\partial^2 f}{\partial\varphi^2}=\lambda f(\varphi,\vartheta)$$

New Hard Problem

The Problem

$$\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial f}{\partial\vartheta}\right)+\frac{1}{\sin^2\vartheta}\frac{\partial^2 f}{\partial\varphi^2}=\lambda f(\varphi,\vartheta)$$

Idea

Separation ansatz:

$$f(\varphi,\vartheta)=\Phi(\varphi)\Theta(\vartheta)$$

From the “easy” part:

$$\frac{d^2\Phi}{d\varphi^2}=\kappa\Phi(\varphi)\implies\Phi(\varphi)=e^{im\varphi},\quad m\in\mathbb{Z}$$

Associated Legendre Differential Equation

Separation (cont.)

The hard part is the ODE for $\Theta(\vartheta)$:

$$\sin^2\vartheta \frac{d^2\Theta}{d(\cos\vartheta)^2} - 2\cos\theta \frac{d\Theta}{d\cos\vartheta} + \left[n(n+1) - \frac{m^2}{\sin^2\vartheta}\right]\Theta(\cos\vartheta) = 0$$

Associated Legendre Differential Equation

Separation (cont.)

The hard part is the ODE for $\Theta(\vartheta)$:

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Substituting $x = \cos\vartheta$ and $y = \Theta$:

Definition (Associated Legendre Differential Equation)

$$\left(1 - x^2\right)\frac{d^2y}{dx^2} - 2x\frac{dy}{dx} + \left[n(n+1) - \frac{m^2}{1-x^2}\right]y(x) = 0$$

Legendre Polynomials

Definition (Legendre Polynomials)

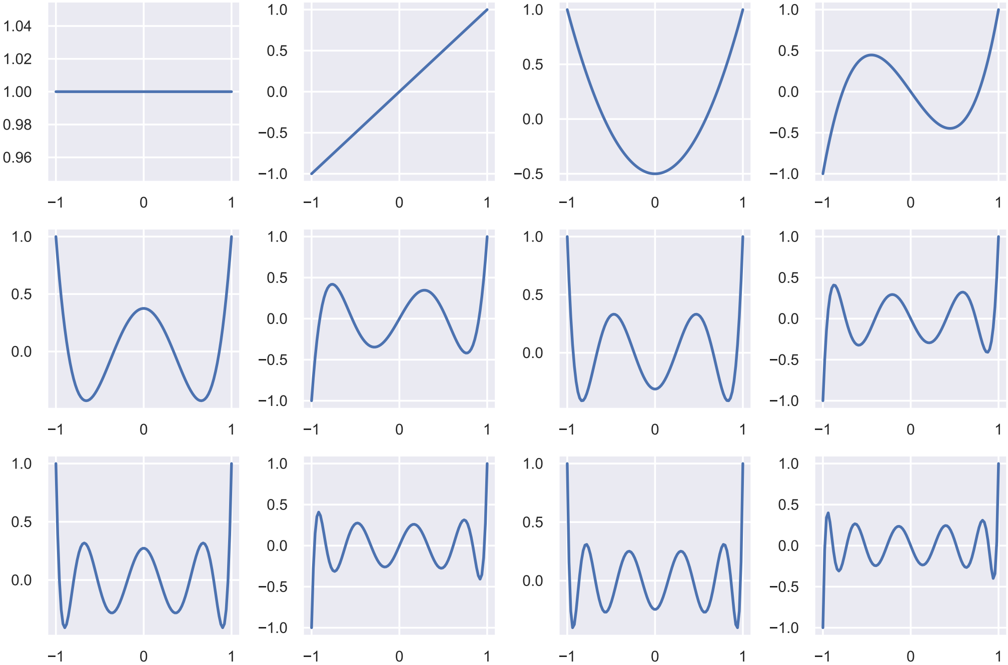
The polynomials

$$P_n(x) = \sum_{k=0}^{\lfloor n/2 \rfloor} \frac{(-1)^k (2n-2k)!}{2^n k!(n-k)!(n-2k)!} x^{n-2k}$$

$$= {}_2F_1\left(\begin{matrix} n+1, & -n \\ & 1 \end{matrix}; \frac{1-x}{2}\right)$$

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

are a solution to the associated Legendre differential equation when $m = 0$.


1.04
1.02
1.00
0.98
0.96
1.0
0.5
0.0
−0.5
−1.0
−1
0
1

Associated Legendre Polynomials

Lemma

For $x \in [-1, 1]$ *the polynomials*

$$P_{m,n}(x) = \left(1 - x^2\right)^{m/2} \frac{d^m}{dx^m} P_n(x)$$

solve the associated Legendre differential equation.

Associated Legendre Polynomials

Lemma

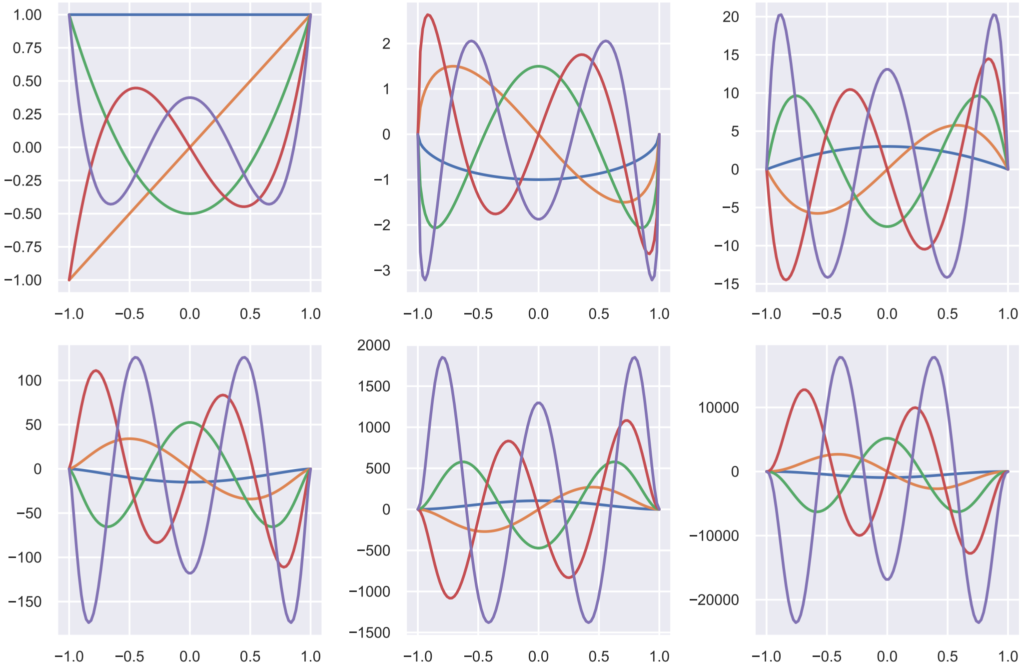
For $x \in [-1, 1]$ *the polynomials*

$$P_{m,n}(x) = \left(1 - x^2\right)^{m/2} \frac{d^m}{dx^m} P_n(x)$$

solve the associated Legendre differential equation.

Observation

If $m > n$ then $P_{m,n}(x) = 0$ for all x.


1.00
0.75
0.50
0.25
0.00
−0.25
−0.50
−0.75
−1.00
−1.0 −0.5 0.0 0.5 1.0
2
1
0
−1
−2
−3
20
15
10
5
0
−5
−10
−15
100
50
0
−50
−100
−150
2000
1500
1000
500
0
−500
−1000
−1500
10000
0
−10000
−20000

Putting it back together

The Problem

$$\nabla_s^2 f(\varphi, \vartheta) = \lambda f(\varphi, \vartheta)$$

Current solution

For $m \in \mathbb{Z}$ and $m < n$:

$$\tilde{Y}_{m,n}(\varphi, \vartheta) = \Phi(\varphi)\Theta(\vartheta) = e^{im\varphi} P_{m,n}(\cos \vartheta)$$

What do they look like?

Python Magic

Intuition of conditions for m and n

Research Question

Recurrence Relation(s)?

$$\tilde{Y}_{m+1,n} \stackrel{?}{=} f(\tilde{Y}_{m,n}, \tilde{Y}_{m-1,n}, \tilde{Y}_{m,n-1}, \ldots)$$

$$\tilde{Y}_{m,n+1} \stackrel{?}{=} f(\tilde{Y}_{m,n}, \tilde{Y}_{m-1,n}, \tilde{Y}_{m,n-1}, \ldots)$$

$$\tilde{Y}_{m+1,n+1} \stackrel{?}{=} f(\tilde{Y}_{m,n}, \tilde{Y}_{m-1,n}, \tilde{Y}_{m,n-1}, \ldots)$$

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Basis functions?

The functions $\tilde{Y}_{m,n}$ span the space of nice functions $S^2 \to \mathbb{C}$.

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The functions $\tilde{Y}_{m,n}$ span the space of nice functions $S^2 \to \mathbb{C}$.

Definition

The inner product of nice functions $f(\varphi, \vartheta)$ and $g(\varphi, \vartheta)$ from S^2 to $\mathbb{C}$ is

$$\langle f, g \rangle = \iint_{S^2} f(\varphi, \vartheta) \overline{g}(\varphi, \vartheta) \, d\Omega$$

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$$\langle f, g \rangle = \iint_{S^2} f(\varphi, \vartheta)\overline{g}(\varphi, \vartheta)\, d\Omega = \int_0^{2\pi} \int_0^{\pi} f(\varphi, \vartheta)\overline{g}(\varphi, \vartheta) \sin\vartheta \, d\vartheta d\varphi$$

Orthonormality

Definition

A set of basis functions are *orthonormal* if

$$\langle B_{m,n}, B_{m',n'} \rangle = \begin{cases} 1 & m = m' \wedge n = n' \\ 0 & \text{else} \end{cases}$$

Orthonormality

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A set of basis functions are *orthonormal* if

$$\langle B_{m,n}, B_{m',n'} \rangle = \begin{cases} 1 & m = m' \wedge n = n' \\ 0 & \text{else} \end{cases}$$

Problem

$$\langle \tilde{Y}_{m,n}, \tilde{Y}_{m',n'} \rangle = \begin{cases} \frac{4\pi}{2n+1} \frac{(n+m)!}{(n-m)!} & m = m' \wedge n = n' \\ 0 & \text{else} \end{cases}$$

Spherical Harmonics

Definition

The orthonormal spherical harmonics are

$$Y_{m,n}(\varphi, \vartheta) = N_{m,n} e^{im\varphi} P_{m,n}(\cos \vartheta)$$

where the normalisation constant

$$N_{m,n} = \sqrt{\frac{2n+1}{4\pi} \frac{(n-m)!}{(n+m)!}}$$

Fixed

$$\langle Y_{m,n}, Y_{m',n'} \rangle = \begin{cases} 1 & m = m' \wedge n = n' \\ 0 & \text{else} \end{cases}$$

Fourier Series

Theorem

For nice periodic functions on S^2:

$$f(\varphi, \vartheta) = \sum_{m \in \mathbb{Z}} \sum_{n \in \mathbb{Z}} c_{m,n} Y_{m,n}(\varphi, \vartheta)$$

where

$$c_{m,n} = \langle f, Y_{m,n} \rangle.$$

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Linear and Rotational Kinetic Energy

Momentum and KE

$$\mathbf{p} = m\mathbf{v}, \quad E_k = \frac{\mathbf{p}^2}{2m}$$

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$$\mathbf{p} = m\mathbf{v}, \quad E_k = \frac{\mathbf{p}^2}{2m}$$

Angular Momentum and KE

$$\mathbf{L} = \mathbf{r} \times \mathbf{p}, \quad E_{k,a} = \frac{\mathbf{L}^2}{2mr^2}$$

Linear and Rotational Kinetic Energy

Momentum and KE

$$\mathbf{p} = m\mathbf{v}, \quad E_k = \frac{\mathbf{p}^2}{2m}$$

QM Formulation

$$\hat{\mathbf{p}} = -i\hbar\boldsymbol{\nabla}, \quad \hat{E}_k = -\frac{\hbar^2}{2m}\nabla^2$$

Angular Momentum and KE

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Linear and Rotational Kinetic Energy

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Angular Momentum and KE

$$\mathbf{L} = \mathbf{r} \times \mathbf{p}, \quad E_{k,a} = \frac{\mathbf{L}^2}{2mr^2}$$

QM Formulation

Pretty long derivation yields:

$$\hat{E}_{k,a} = -\frac{\hbar^2}{2mr^2}\nabla_s^2$$

Intuition for the Operators

Schrödinger Equation

Time independent SE

$$\hat{\mathcal{H}}|\Psi\rangle = E|\Psi\rangle$$

Schrödinger Equation

Time independent SE

$$\left(\hat{E}_k + U\right)|\Psi\rangle = E|\Psi\rangle$$

Schrödinger Equation

Time independent SE

$$\left(\frac{\hat{\mathbf{p}}^2}{2m} + U\right)|\Psi\rangle = E|\Psi\rangle$$

Schrödinger Equation

Time independent SE

Meili $$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+U(x)\right]\Psi(x)=E\Psi(x)$$

Schrödinger Equation

Time independent SE

3D

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{x})\right]\Psi(\mathbf{x}) = E\Psi(\mathbf{x})$$

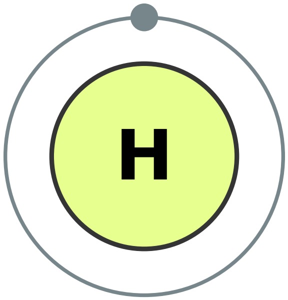
Schrödinger Equation

Time independent SE

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

But why?

Hydrogen atom has radial symmetry!



Schrödinger Equation

Time independent SE

$$\left[\frac{\hat{\mathbf{L}}^2}{2mr^2} + \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + U(\mathbf{r})\right]\Psi(\mathbf{r}) = E\Psi(\mathbf{r})$$

Schrödinger Equation

Time independent SE

$$\left[\hat{E}_{k,a} + \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + U(\mathbf{r})\right]\Psi(\mathbf{r}) = E\Psi(\mathbf{r})$$

Schrödinger Equation

Time independent SE

$$\left[\underbrace{\hat{E}_{k,a} + \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)}_{\text{Kinetic Energy}} + U(\mathbf{r})\right]\Psi(\mathbf{r}) = E\Psi(\mathbf{r})$$

Schrödinger Equation

Time independent SE

$$\left[\hat{E}_{k,a} + \underbrace{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)}_{\text{Radial KE } \hat{E}_{k,r}} + U(\mathbf{r})\right]\Psi(\mathbf{r}) = E\Psi(\mathbf{r})$$

Schrödinger Equation

Time independent SE

$$\left\{\hat{E}_{k,a} + \hat{E}_{k,r} + U(\mathbf{r})\right\} \Psi(\mathbf{r}) = E\Psi(\mathbf{r})$$

Electron Orbitals

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