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# Hydrogen Atom: The Inspiration

Iridium LINCH-SK

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# Schrödinger Eqn.

- 3D Occasion, Cartesian coordinate:

$$\left(-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+V(\boldsymbol{r})\right)\psi = E\psi$$

- But a centered potential: $V(\boldsymbol{r}) = V(r)$
- It seems that a cartesian coordinate can't handle such problems.

# Syllabus

- Nabla (In points of orthogonal curvilinear coordinates)
  - Laplace
- Hydrogen Atom
  - Angular Equations
  - Sturm-Liouville Systems

# Spherical Coordinates

$$\begin{cases} r = \sqrt{x^2 + y^2 + z^2}, \\ \theta = \arccos \dfrac{z}{\sqrt{x^2 + y^2 + z^2}}, \\ \varphi = \arctan \dfrac{y}{x}. \end{cases} \quad \begin{cases} x = r \sin\theta \cos\varphi, \\ y = r \sin\theta \sin\varphi, \\ z = r \cos\varphi. \end{cases}$$

# Laplace, but Nabla first

- We have to understand a Nabla to better understand a Laplace.

$$\boldsymbol{E} = -\nabla \varphi,$$

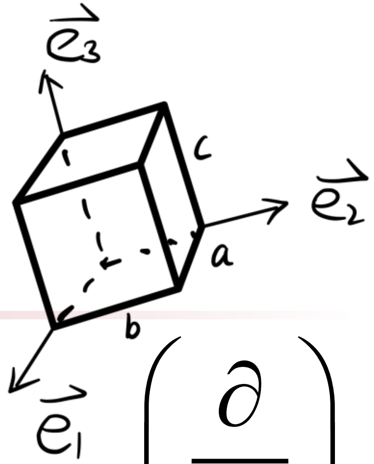
$$\nabla \cdot \boldsymbol{B} = 0,$$

$$\nabla \times \boldsymbol{E} = -\frac{\partial}{\partial t}\boldsymbol{B},$$

$$\left( \frac{1}{c^2} \frac{\partial^2}{\partial t^2} - \nabla^2 \right) \boldsymbol{E} = 0.$$

$$\nabla^2 = \nabla \cdot \nabla$$

# Gradient: The simplest Nabla




- Cartesian gradient: the most trivial nabla
  - **Global** operator
- How to represent nabla explicitly in other coordinates?
- **Localized** operator
  - Local coordinate
  - Orthogonality
- Change the representation to avoid misunderstanding:

$$\nabla = \begin{pmatrix} \frac{\partial}{\partial x} \\ \frac{\partial}{\partial y} \\ \frac{\partial}{\partial z} \end{pmatrix}$$

$$\nabla = \boldsymbol{e}_x \frac{\partial}{\partial x} + \boldsymbol{e}_y \frac{\partial}{\partial y} + \boldsymbol{e}_z \frac{\partial}{\partial z} = \boldsymbol{e}_1 \frac{\partial}{\partial a} + \boldsymbol{e}_2 \frac{\partial}{\partial b} + \boldsymbol{e}_3 \frac{\partial}{\partial c}$$

# Orthogonal Curvilinear Coordinates

- Why such name?
  - Curve: Pile up tiny bricks, then there are curves.

# Orthogonal Curvilinear Coordinates

- In terms of using, the coordinate is often not identical to *a*, *b*, *c*.

$$(\mathrm{d})a = h_1 \mathrm{d}q_1,$$
$$(\mathrm{d})b = h_2 \mathrm{d}q_2,$$
$$(\mathrm{d})c = h_3 \mathrm{d}q_3.$$

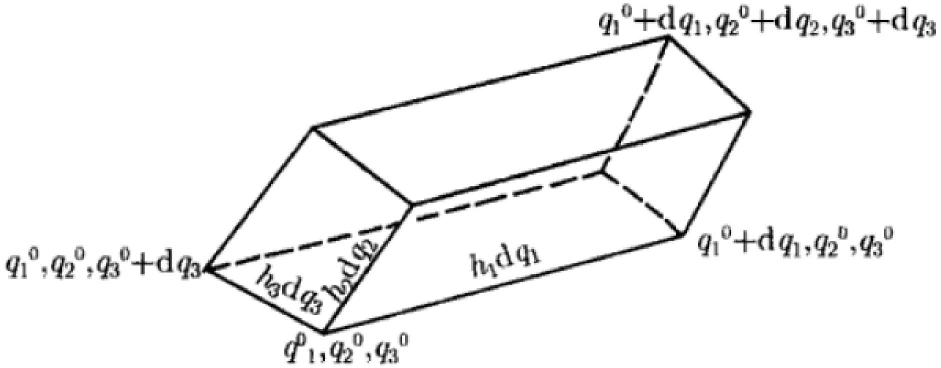


图 9.2.1　广义坐标系中的体积元

- The *h*s are called Lamé coefficients.

# Nabla in OCLC

- The nabla in terms of Lamé coefficients and OCLC.

$$\nabla = \boldsymbol{e}_1 \frac{1}{h_1} \frac{\partial}{\partial q_1} + \boldsymbol{e}_2 \frac{1}{h_2} \frac{\partial}{\partial q_2} + \boldsymbol{e}_3 \frac{1}{h_3} \frac{\partial}{\partial q_3}$$

- And the Laplace:

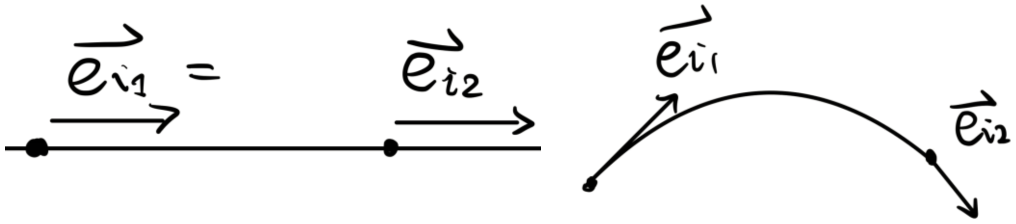
$$\nabla^2 = \nabla \cdot \nabla = \left( \boldsymbol{e}_1 \frac{1}{h_1} \frac{\partial}{\partial q_1} + \boldsymbol{e}_2 \frac{1}{h_2} \frac{\partial}{\partial q_2} + \boldsymbol{e}_3 \frac{1}{h_3} \frac{\partial}{\partial q_3} \right) \cdot \left( \boldsymbol{e}_1 \frac{1}{h_1} \frac{\partial}{\partial q_1} + \boldsymbol{e}_2 \frac{1}{h_2} \frac{\partial}{\partial q_2} + \boldsymbol{e}_3 \frac{1}{h_3} \frac{\partial}{\partial q_3} \right)$$

# Nabla in OCLC

- Here comes a problem:

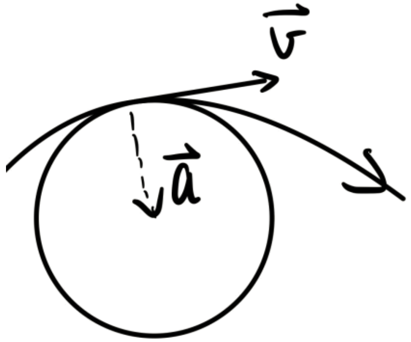
$$\frac{\partial}{\partial q_i}\boldsymbol{e}_j = ?\left(i, j = 1, 2, 3.\right)$$

- In Xu G.X.'s textbook, this problem was bypassed via a hydrodynamic view that directly give the form of Laplace in terms of OCLC and Lamé coefficients. (Section 9.2.4 in Volume II)
- However I'd like to introduce a new and intuitive method to solve the problem and give Laplace, i.e. Curvature view.




# Curvature View

- If the curve $q_j$, $q_k$ = const. is straight, then such partial derivative is 0.
- If the partial derivative is nonzero, then the curve must curl, thus have a curvature.
- A radius of curvature can be defined intuitively by considering the velocity and acceleration of an mass point:



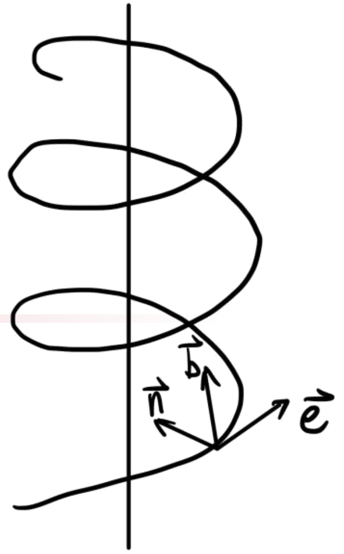

$$r = \frac{v^2}{a} = \frac{\left|\frac{\mathrm{d}\boldsymbol{r}}{\mathrm{d}t}\right|^2}{\left|\frac{\mathrm{d}^2\boldsymbol{r}}{\mathrm{d}t^2}\right|}$$

# Curvature: In terms of natural coordinate

- Assume that the particle is moving with a constant speed *v*, then curvature can be represented in a natural coordinate, i.e. path of motion.

$$r = \frac{v^2}{\left|\frac{\mathrm{d}^2\boldsymbol{r}}{\mathrm{d}t^2}\right|} = \frac{1}{\left|\frac{\mathrm{d}^2\boldsymbol{r}}{\mathrm{d}l^2}\right|}; \kappa = \frac{1}{r} = \left|\frac{\mathrm{d}^2\boldsymbol{r}}{\mathrm{d}l^2}\right|$$

# Direction of Curvature



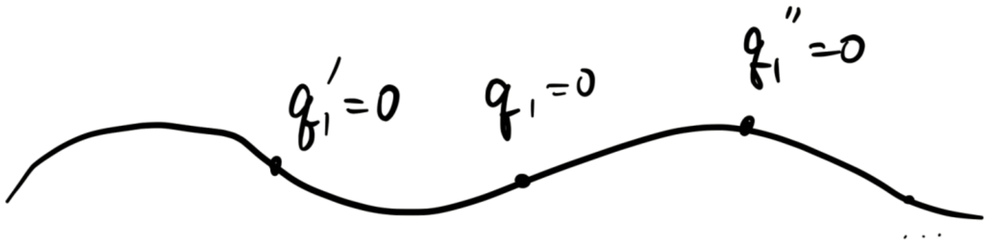

- Curvature can be defined as a vector, and the unit vector parallel to curvature vector is always perpendicular to the tangent unit vector.

$$\frac{\mathrm{d}\boldsymbol{r}}{\mathrm{d}l}=\boldsymbol{e},\frac{\mathrm{d}^2\boldsymbol{r}}{\mathrm{d}l^2}=\frac{\mathrm{d}\boldsymbol{e}}{\mathrm{d}l}=\kappa\boldsymbol{n},0=\frac{\mathrm{d}\left(\boldsymbol{e}^2\right)}{\mathrm{d}l}=2\boldsymbol{e}\cdot\frac{\mathrm{d}\boldsymbol{e}}{\mathrm{d}l}=2\kappa\boldsymbol{e}\cdot\boldsymbol{n}=0.$$

- Introduce the torsion unit vector to form a complete basis for the local curvilinear coordinate:

$$\boldsymbol{e}\times\boldsymbol{n}=:\boldsymbol{b}$$

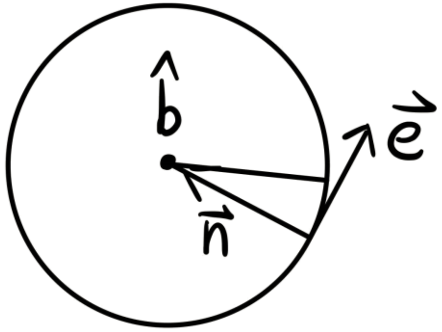
# Direction of Curvature




- Now we have:

$$\frac{\partial}{\partial q_i}\boldsymbol{e}_i = \frac{\partial\left(h_i q_i\right)}{\partial q_i}\frac{\partial}{\partial\left(h_i q_i\right)}\boldsymbol{e}_i = \left(h_i + q_i\frac{\partial h_i}{\partial q_i}\right)\kappa\boldsymbol{n}_i$$

- We can always assign that $q_i$ = 0, since it is all about picking which point on the curve $q_j$, $q_k$ = const. as the origin.
- All $\mathbf{e}_j$ are actually rotating around the torsion unit vector:

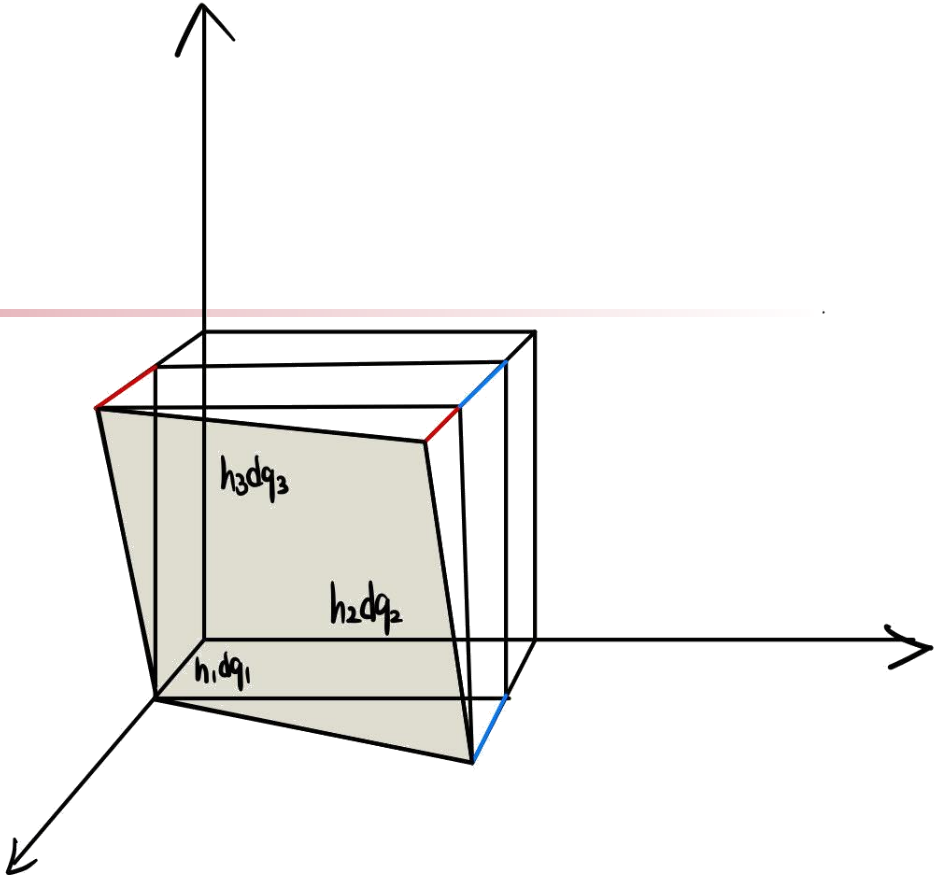


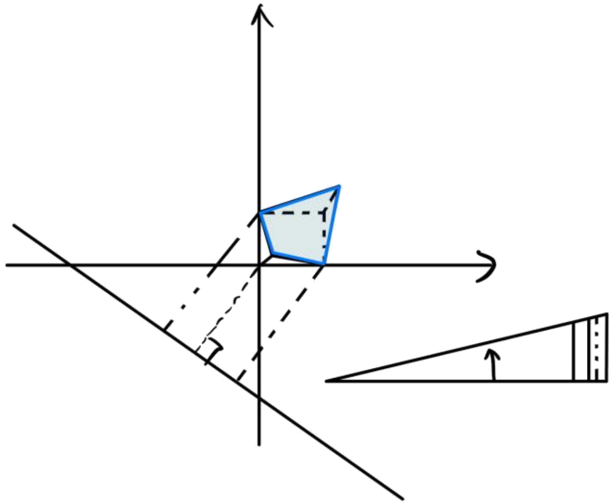

$$\boldsymbol{b}\kappa h_i \mathrm{d}q_i \times \boldsymbol{e}_i = \kappa h_i \mathrm{d}q_i \boldsymbol{n} = \mathrm{d}q_i \frac{\partial}{\partial q_i}\boldsymbol{e}_i$$

$$\kappa h_i \mathrm{d}q_i\left(\boldsymbol{e}_i \times \boldsymbol{n}\right)\times\boldsymbol{e}_j = \mathrm{d}q_i\frac{\partial}{\partial q_i}\boldsymbol{e}_j$$

# Direction of Curvature

- Where do $\boldsymbol{n}_i$ orient?
- Take $\boldsymbol{n}_1$ as an example.
  - Red lines: $\dfrac{\partial h_1}{\partial q_3}\mathrm{d}q_3\mathrm{d}q_1$
  - Blue lines: $\dfrac{\partial h_1}{\partial q_2}\mathrm{d}q_2\mathrm{d}q_1$



$$\begin{cases} A = h_1\mathrm{d}q_1 + \dfrac{\partial h_1}{\partial q_2}\dfrac{\mathrm{d}q_1}{h_2}B + \dfrac{\partial h_1}{\partial q_3}\dfrac{\mathrm{d}q_1}{h_3}C, \\ A = 0. \end{cases}$$

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# Curvature Vector

- The intersection line have equation:

$$0 = h_1 \mathrm{d}q_1 + \frac{\partial h_1}{\partial q_2}\frac{\mathrm{d}q_1}{h_2}B + \frac{\partial h_1}{\partial q_3}\frac{\mathrm{d}q_1}{h_3}C$$

- Distance of the origin to the intersection line of two planes, i.e. radius of curvature:

$$\frac{h_1}{\sqrt{\left(\frac{\partial h_1}{\partial q_2}\frac{1}{h_2}\right)^2 + \left(\frac{\partial h_1}{\partial q_3}\frac{1}{h_3}\right)^2}}$$

# Curvature Vector

- Normal vector (from origin to the intersection line):

$$\left(0, -\frac{\partial h_1}{\partial q_2}\frac{1}{h_2}, -\frac{\partial h_1}{\partial q_3}\frac{1}{h_3}\right)$$

- Curvature vector:

$$\left(0, -\frac{\partial h_1}{\partial q_2}\frac{1}{h_1 h_2}, -\frac{\partial h_1}{\partial q_3}\frac{1}{h_1 h_3}\right)$$

# Final Form of vectors' partial derivatives

$$\frac{\partial}{\partial q_1}\boldsymbol{e}_1 = \kappa h_1\left(\boldsymbol{e}_1 \times \boldsymbol{n}\right)\times \boldsymbol{e}_1 = -\frac{1}{h_2}\frac{\partial h_1}{\partial q_2}\boldsymbol{e}_2 - \frac{1}{h_3}\frac{\partial h_1}{\partial q_3}\boldsymbol{e}_3$$

$$\frac{\partial}{\partial q_1}\boldsymbol{e}_2 = \kappa h_1\left(\boldsymbol{e}_1 \times \boldsymbol{n}\right)\times \boldsymbol{e}_2 = \frac{1}{h_2}\frac{\partial h_1}{\partial q_2}\boldsymbol{e}_2$$

$$\frac{\partial}{\partial q_1}\boldsymbol{e}_3 = \kappa h_1\left(\boldsymbol{e}_1 \times \boldsymbol{n}\right)\times \boldsymbol{e}_3 = \frac{1}{h_2}\frac{\partial h_1}{\partial q_2}\boldsymbol{e}_3$$

# Final Form of vectors’ partial derivatives

$$\frac{\partial}{\partial q_2}\boldsymbol{e}_1=\kappa h_2\left(\boldsymbol{e}_2\times\boldsymbol{n}\right)\times\boldsymbol{e}_1=\frac{1}{h_1}\frac{\partial h_2}{\partial q_1}\boldsymbol{e}_2$$

$$\frac{\partial}{\partial q_2}\boldsymbol{e}_2=\kappa h_2\left(\boldsymbol{e}_2\times\boldsymbol{n}\right)\times\boldsymbol{e}_2=-\frac{1}{h_1}\frac{\partial h_2}{\partial q_1}\boldsymbol{e}_1-\frac{1}{h_3}\frac{\partial h_2}{\partial q_3}\boldsymbol{e}_3$$

$$\frac{\partial}{\partial q_2}\boldsymbol{e}_3=\kappa h_2\left(\boldsymbol{e}_2\times\boldsymbol{n}\right)\times\boldsymbol{e}_3=\frac{1}{h_3}\frac{\partial h_2}{\partial q_3}\boldsymbol{e}_3$$

# Final Form of vectors' partial derivatives

$$\frac{\partial}{\partial q_3}\boldsymbol{e}_1 = \kappa h_1\left(\boldsymbol{e}_3 \times \boldsymbol{n}\right)\times \boldsymbol{e}_1 = \frac{1}{h_1}\frac{\partial h_3}{\partial q_1}\boldsymbol{e}_3$$

$$\frac{\partial}{\partial q_3}\boldsymbol{e}_2 = \kappa h_1\left(\boldsymbol{e}_3 \times \boldsymbol{n}\right)\times \boldsymbol{e}_2 = \frac{1}{h_2}\frac{\partial h_3}{\partial q_2}\boldsymbol{e}_3$$

$$\frac{\partial}{\partial q_2}\boldsymbol{e}_3 = \kappa h_1\left(\boldsymbol{e}_3 \times \boldsymbol{n}\right)\times \boldsymbol{e}_3 = -\frac{1}{h_1}\frac{\partial h_3}{\partial q_1}\boldsymbol{e}_1 - \frac{1}{h_2}\frac{\partial h_3}{\partial q_2}\boldsymbol{e}_2$$

# Laplace in OCLC

$$\left(\boldsymbol{e}_1\frac{1}{h_1}\frac{\partial}{\partial q_1}+\boldsymbol{e}_2\frac{1}{h_2}\frac{\partial}{\partial q_2}+\boldsymbol{e}_3\frac{1}{h_3}\frac{\partial}{\partial q_3}\right)\cdot\boldsymbol{e}_1\frac{1}{h_1}\frac{\partial}{\partial q_1}$$

- Consider only the first term.

$$=\frac{1}{h_1}\frac{\partial}{\partial q_1}\left(\frac{1}{h_1}\frac{\partial}{\partial q_1}\right)+\boldsymbol{e}_2\frac{1}{h_2}\frac{\partial \boldsymbol{e}_1}{\partial q_2}\frac{1}{h_1}\frac{\partial}{\partial q_1}+\boldsymbol{e}_3\frac{1}{h_3}\frac{\partial \boldsymbol{e}_1}{\partial q_3}\frac{1}{h_1}\frac{\partial}{\partial q_1}$$

$$=\frac{1}{h_1}\frac{\partial}{\partial q_1}\left(\frac{1}{h_1}\frac{\partial}{\partial q_1}\right)+\frac{1}{h_2}\frac{1}{h_1}\frac{\partial h_2}{\partial q_1}\frac{1}{h_1}\frac{\partial}{\partial q_1}+\frac{1}{h_3}\frac{1}{h_1}\frac{\partial h_3}{\partial q_1}\frac{1}{h_1}\frac{\partial}{\partial q_1}$$

$$=\frac{1}{h_1h_2h_3}\left(h_2h_3\frac{\partial}{\partial q_1}\left(\frac{1}{h_1}\frac{\partial}{\partial q_1}\right)+h_3\frac{\partial h_2}{\partial q_1}\frac{1}{h_1}\frac{\partial}{\partial q_1}+h_2\frac{\partial h_3}{\partial q_1}\frac{1}{h_1}\frac{\partial}{\partial q_1}\right)$$

$$=\frac{1}{h_1h_2h_3}\left(h_2h_3\frac{\partial}{\partial q_1}\left(\frac{1}{h_1}\frac{\partial}{\partial q_1}\right)+\frac{\partial\left(h_2h_3\right)}{\partial q_1}\frac{1}{h_1}\frac{\partial}{\partial q_1}\right)$$

$$=\frac{1}{h_1h_2h_3}\frac{\partial}{\partial q_1}\left(\frac{h_2h_3}{h_1}\frac{\partial}{\partial q_1}\right)$$

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# Laplace in OCLC

- The Final Form:

$$\nabla^2 = \frac{1}{h_1 h_2 h_3}\left(\frac{\partial}{\partial q_1}\left(\frac{h_2 h_3}{h_1}\frac{\partial}{\partial q_1}\right)+\frac{\partial}{\partial q_2}\left(\frac{h_1 h_3}{h_2}\frac{\partial}{\partial q_2}\right)+\frac{\partial}{\partial q_3}\left(\frac{h_1 h_2}{h_3}\frac{\partial}{\partial q_3}\right)\right)$$

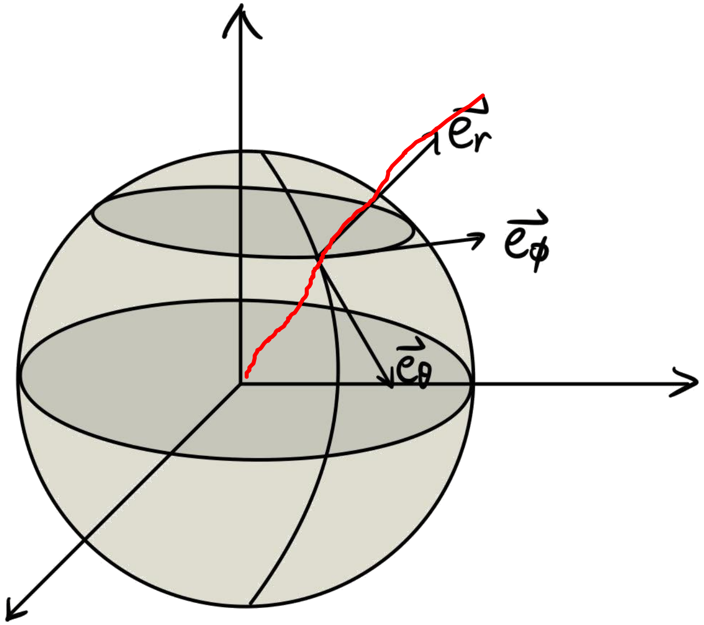
# Spherical Coordinates as OCLC

- Lamé coefficients:

$$h_1 := h_r = 1,$$

$$h_2 := h_\theta = r,$$

$$h_3 := h_\phi = r \sin\theta.$$




- Laplace:

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

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# Hydrogen Atom: Central Potential First

- Tiny notations make a difference:

$$\left(-\frac{\hbar^2}{2m}\nabla^2+V(\boldsymbol{r})\right)\psi=E\psi\cdots$$

$$\left(-\frac{\hbar^2}{2m}\nabla^2+V(r)\right)\psi=E\psi!$$

- 传统艺能：Variable separation!

$$\left(-\frac{\hbar^2}{2m}\nabla^2+V(r)\right)R(r)Y(\theta,\phi)=ER(r)Y(\theta,\phi),$$

$$\left(-\frac{\hbar^2}{2m}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)+V(r)\right)R(r)Y(\theta,\phi)=ER(r)Y(\theta,\phi).$$

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# Central Potential: Variable Separation

- Write all terms in form of separated variables, then absorb them into coefficients.

$$-\frac{\hbar^2}{2m}\left(Y(\theta,\phi)R_1(r)+\frac{R_2(r)}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y(\theta,\phi)}{\partial\theta}\right)+\frac{R_2(r)}{\sin^2\theta}\frac{\partial^2 Y(\phi)}{\partial\phi^2}\right)+V(r)R(r)Y(\theta,\phi)=ER(r)Y(\theta,\phi)$$

$$R_1(r)=\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right)$$

$$R_2(r)=\frac{R(r)}{r^2}$$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y(\theta,\phi)}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y(\theta,\phi)}{\partial\phi^2}=E_Y Y(\theta,\phi)$$

$$-\frac{1}{R_2(r)}\left(\frac{2m}{\hbar^2}\left(E-V(r)\right)R(r)+R_1(r)\right)=:E_Y$$

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# Angular Equation: VS again.

- The Angular Equation can be variable-separated again.

$$\frac{\Phi(\phi)}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta(\theta)}{\partial\theta}\right)+\frac{\Theta(\theta)}{\sin^2\theta}\frac{\partial^2\Phi(\phi)}{\partial\phi^2}=E_Y\Theta(\theta)\Phi(\phi)$$

$$\Theta_1(\theta)\Phi(\phi)+\Theta_2(\theta)\frac{\partial^2\Phi(\phi)}{\partial\phi^2}=E_Y\Theta(\theta)\Phi(\phi)$$

$$\Theta_1(\theta)=\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta(\theta)}{\partial\theta}\right)$$

$$\Theta_2(\theta)=\frac{\Theta(\theta)}{\sin^2\theta}$$

$$\frac{\mathrm{d}^2\Phi(\phi)}{\mathrm{d}\phi^2}=\frac{E_Y\Theta(\theta)-\Theta_1(\theta)}{\Theta_2(\theta)}\Phi(\phi)=E_\Phi\Phi(\phi)$$

$$\frac{1}{\sin\theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}\Theta(\theta)}{\mathrm{d}\theta}\right)+\frac{\Theta(\theta)}{\sin^2\theta}E_\Phi=E_Y\Theta(\theta)$$

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# Φ: Solutions

- Cyclic boundary condition: $\Phi(\phi)=\Phi(\phi+2\pi)$

$$\frac{\mathrm{d}^2\Phi(\phi)}{\mathrm{d}\phi^2}=E_\Phi\Phi(\phi)$$

$$\Phi(\phi)=\mathrm{e}^{\sqrt{E_\Phi}\phi}=\mathrm{e}^{\sqrt{E_\Phi}(\phi+2\pi)}$$

$$\mathrm{e}^{2\pi\sqrt{E_\Phi}}=1$$

$$\sqrt{E_\Phi}=\mathrm{i}m,(m\in\mathbf{Z});E_\Phi=-m^2,(m\in\mathbf{Z}).$$

- The Φ equation and solutions actually have such a form:

$$\frac{\mathrm{d}^2\Phi(\phi)}{\mathrm{d}\phi^2}=-m^2\Phi(\phi),\Phi(\phi)=\mathrm{e}^{\mathrm{i}m\phi},(m\in\mathbf{Z})$$

# Θ: Something more complex

- Substitute $d^2\Phi/d\varphi^2$ by Φ according to the Φ Equation, we have the Θ Equation:

$$\frac{1}{\sin\theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}\Theta(\theta)}{\mathrm{d}\theta}\right)+\left(-E_Y-\frac{m^2}{\sin^2\theta}\right)\Theta(\theta)=0$$

- It's not easy to figure out $E_Y$ and the solutions rather than the Φ Equation, in which we can find the solutions are Fourier basis in one glance.
- Substitute the variable:

$$\frac{\mathrm{d}}{\mathrm{d}x}\left(\left(1-x^2\right)\frac{\mathrm{d}y}{\mathrm{d}x}\right)+\left(-E_Y-\frac{m^2}{1-x^2}\right)y=0,$$

$$x=\cos\theta.$$

# Sturm-Liouville System: A General Way to Consider 2-order ODEs

- 代（Substitute）数: As long as some kind of relationship can be established, one can substitute the general form by a specified object to observe its properties. Quoted from Iridium LINCH-SK.

$$\mathbf{L}u = \left( p_2(x)\frac{\mathrm{d}^2}{\mathrm{d}x^2} + p_1(x)\frac{\mathrm{d}}{\mathrm{d}x} + p_0(x) \right) u$$

- **L** is a linear operator, which means we can apply linear algebra on it. Consider an inner product

$$\langle v | u \rangle = \int_a^b \mathrm{d}x v^*(x) u(x)$$

# Hermitian in Sturm-Liouville System:

- We can define a “conjugated transpose”:

$$v^*\mathbf{L}u = v^* p_2 u'' + v^* p_1 u' + v^* p_0 u$$

$$= p_2\left(u'v^*\right)' - p_2 u' v^{*\prime} + p_1\left(uv^*\right)' - p_1 u v^{*\prime} + u p_0 v^*$$

$$= p_2\left(u'v^* - uv^{*\prime}\right)' + u p_2 v^{*\prime\prime} + p_1\left(uv^*\right)' - p_1 u v^{*\prime} + u p_0 v^*$$

$$= \left(p_2\left(u'v^* - uv^{*\prime}\right)\right)' - p_2'\left(u'v^* - uv^{*\prime}\right) + u p_2 v^{*\prime\prime} + \left(p_1 u v^*\right)' - u p_1' v^* - p_1 u v^{*\prime} + u p_0 v^*$$

$$= u p_2 v^{*\prime\prime} + 2u p_2' v^{*\prime} - p_1 u v^{*\prime} - u p_1' v^* + u p_0 v^* + u p_2'' v^* + \left(p_2\left(u'v^* - uv^{*\prime}\right)\right)' + \left(p_1 u v^*\right)' - \left(p_2' u v^*\right)'$$

$$= \left(u^*\mathbf{M}v + \left(p_2^*\left(u^{*\prime} v - u^* v'\right) + p_1 u^* v - p_2^{*\prime} u^* v\right)'\right)^*$$

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# Hermitian in Sturm-Liouville System:

- Here:

$$\mathbf{M}=\left(p_2\frac{\mathrm{d}^2}{\mathrm{d}x^2}+\left(2p_2'-p_1\right)\frac{\mathrm{d}}{\mathrm{d}x}+p_2''-p_1'+p_0\right)^*$$

- And we have a total differential as the last term.
- Let's move on to the inner products, which are integrals of $v^*\mathbf{L}u$ or $u^*\mathbf{M}v$:

$$\langle v|\mathbf{L}|u\rangle=\langle u^*|\mathbf{M}|v\rangle^*+\left(p_2^*\left(u^*{}'v-u^*v'\right)+p_1u^*v-p_2^*{}'u^*v\right)^*\Big|_a^b$$

- In fact, the second term often vanishes according to boundary conditions.

# Hermitian in Sturm-Liouville System:

- Hermitian means that:

$$\mathbf{M}=\left(p_2\frac{\mathrm{d}^2}{\mathrm{d}x^2}+\left(2p_2'-p_1\right)\frac{\mathrm{d}}{\mathrm{d}x}+p_2''-p_1'+p_0\right)^*=\mathbf{L}$$

- That is:

$$p_0=p_0^*,$$
$$p_2=p_2^*,$$
$$p_1=p_2'.$$

- Then:

$$\mathbf{M}=\mathbf{L}=\frac{\mathrm{d}}{\mathrm{d}x}\left(p_2\frac{\mathrm{d}}{\mathrm{d}x}\right)+p_0$$

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# Hermitian in Sturm-Liouville System:

- An Hermitian have only real eigenvalues:

$$\lambda^* \langle v | v \rangle = \langle v | \mathbf{L} | v \rangle^* = \langle v | \mathbf{L} | v \rangle = \lambda \langle v | v \rangle$$

- In Sturm-Liouville systems, no degeneracy will occur:

$$\left[ -\frac{\mathrm{d}}{\mathrm{d}x} \left( p \frac{\mathrm{d}}{\mathrm{d}x} \right) + q \right] y_1 = \lambda \rho y_1, \left[ -\frac{\mathrm{d}}{\mathrm{d}x} \left( p \frac{\mathrm{d}}{\mathrm{d}x} \right) + q \right] y_2 = \lambda \rho y_2;$$

$$y_1 \frac{\mathrm{d}}{\mathrm{d}x} \left( p \frac{\mathrm{d}y_2}{\mathrm{d}x} \right) = y_2 \frac{\mathrm{d}}{\mathrm{d}x} \left( p \frac{\mathrm{d}y_1}{\mathrm{d}x} \right)$$

$$\frac{\mathrm{d}}{\mathrm{d}x} \left( y_1 p y_2 ' \right) - y_1 ' p y_2 ' = \frac{\mathrm{d}}{\mathrm{d}x} \left( y_2 p y_1 ' \right) - y_2 ' p y_1 '$$

$$y_1 y_2 ' = y_2 y_1 '$$

$$\frac{y_1}{y_2} = C$$

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# Hermitian in Sturm-Liouville System:

- In Sturm-Liouville systems, all eigenvalues are positive:
- Here, *p*, *q*, *ρ* are all positive.

$$\left[-\frac{\mathrm{d}}{\mathrm{d}x}\left(p\frac{\mathrm{d}}{\mathrm{d}x}\right)+q\right]y=\lambda\rho y$$

$$\int_a^b \mathrm{d}x\left[-\frac{\mathrm{d}}{\mathrm{d}x}\left(p\frac{\mathrm{d}}{\mathrm{d}x}\right)+q\right]y^2=\lambda\int_a^b \mathrm{d}x\rho y^2$$

$$\lambda\int_a^b \mathrm{d}x\rho y^2=\int_a^b \mathrm{d}x\left[-\frac{\mathrm{d}}{\mathrm{d}x}\left(p\frac{\mathrm{d}y}{\mathrm{d}x}\right)\right]y+\int_a^b \mathrm{d}xqy^2$$

$$=\int_a^b \mathrm{d}xqy^2+\int_a^b \mathrm{d}xp\left(\frac{\mathrm{d}y}{\mathrm{d}x}\right)^2>0$$

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# Hermitian in Sturm-Liouville Systems:

- Eigenfunctions with different eigenvalues are weighted orthogonal to each other.

$$\langle v|\mathbf{L}|u\rangle = \langle v|\lambda_1|u\rangle = \langle v|\lambda_2|u\rangle, \langle v|u\rangle = 0.$$

$$\left[-\frac{\mathrm{d}}{\mathrm{d}x}\left(p\frac{\mathrm{d}}{\mathrm{d}x}\right)+q\right]y = \lambda\rho y, \mathbf{L}y = \left[\frac{\mathrm{d}}{\mathrm{d}x}\left(p\frac{\mathrm{d}}{\mathrm{d}x}\right)+(\lambda\rho-q)\right]y = 0.$$

$$p_2 = p, p_0 = \lambda\rho - q.$$

$$\int_a^b \mathrm{d}x vLu = \int_a^b \mathrm{d}x v\left[\frac{\mathrm{d}}{\mathrm{d}x}\left(p\frac{\mathrm{d}}{\mathrm{d}x}\right)+(\lambda\rho-q)\right]u = 0$$

$$\int_a^b \mathrm{d}x v\left[-\frac{\mathrm{d}}{\mathrm{d}x}\left(p\frac{\mathrm{d}}{\mathrm{d}x}\right)+q\right]u = \lambda\int_a^b \mathrm{d}x v\rho u$$

$$\int_a^b \mathrm{d}x v\rho u = 0$$

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# Back to Θ equation

- One will recognize what Θ equation is like under the view of SL systems:

$$\frac{\mathrm{d}}{\mathrm{d}x}\left(\left(1-x^2\right)\frac{\mathrm{d}y}{\mathrm{d}x}\right)+\left(-E_Y-\frac{m^2}{1-x^2}\right)y=0, x=\cos\theta; p=1-x^2, q=\frac{m^2}{1-x^2}, \rho=1.$$

- And the inner product defined on [-1,1] is:

$$\left\langle f_1(x) \mid f_2(x)\right\rangle=\int_{-1}^{1}\mathrm{d}x f_1(x) f_2(x)$$

- Gram-Schmidt Orthogonalization Procedure: To remove any parallel components of known vectors from an unknown vector.

$$\boldsymbol{b}'=\boldsymbol{b}-\frac{\boldsymbol{a}\cdot\boldsymbol{b}}{a^2}\boldsymbol{a}$$

# Legendre Polynomials

- For a series: 1, $x$, $x^2$, $x^3$, …, we can apply GSOP, in which the inner product is defined as in order, and we have such polynomials: 1, $x$, $x^2-1/3$, $x^3-3/5x$, …, denoted in $\mathrm{P}_l(x)$, called Legendre polynomials.
- In fact, such polynomials are solutions of the equation with $m$ = 0, with eigenvalues 0, 2, 6, …, $l(l+1)$, ….

$$\left(1-x^2\right)\frac{\mathrm{d}^2}{\mathrm{d}x^2}\mathrm{P}_l-2x\frac{\mathrm{d}}{\mathrm{d}x}\mathrm{P}_l+E_Y\mathrm{P}_l=0.$$

# Eigenvalues of Legendre Polynomials

- For $P_l(x)$, it contains a nonzero $x^l$ term, which pulls $P_l(x)$ out of the subspace spanned by lower order polynomials, $P_0(x)$ to $P_{l-1}(x)$.

$$\left(1-x^2\right)l\left(l-1\right)x^{l-2}-2xlx^{l-1}-E_Y x^l,$$

$$-l\left(l-1\right)x^l-2lx^l-E_Y x^l=0,$$

$$E_Y=-l\left(l+1\right).$$

# Associated Legendre Functions

- Associated Legendre functions are defined as follow:

$$\mathrm{P}_l^m(x) := \left(\sqrt{1-x^2}\right)^m \frac{\mathrm{d}^m}{\mathrm{d}x^m} \mathrm{P}_l(x)$$

- If we apply ALF into such a formula:

$$\left(1-x^2\right)\frac{\mathrm{d}^2}{\mathrm{d}x^2}\left(\left(\sqrt{1-x^2}\right)^m \frac{\mathrm{d}^m}{\mathrm{d}x^m}\mathrm{P}_l\right) - 2x\frac{\mathrm{d}}{\mathrm{d}x}\left(\left(\sqrt{1-x^2}\right)^m \frac{\mathrm{d}^m}{\mathrm{d}x^m}\mathrm{P}_l\right) + l(l+1)\left(\sqrt{1-x^2}\right)^m \frac{\mathrm{d}^m}{\mathrm{d}x^m}\mathrm{P}_l$$

$$=: A + B + C$$

# Associated Legendre Functions

- In which, $A$ is:

$$\left(1-x^2\right)\frac{d^2}{dx^2}\left(\left(\sqrt{1-x^2}\right)^m\frac{d^m}{dx^m}P_l\right)=\left(\sqrt{1-x^2}\right)^m\left(1-x^2\right)\frac{d^{m+2}}{dx^{m+2}}P_l+2\frac{d}{dx}\left(\sqrt{1-x^2}\right)^m\left(1-x^2\right)\frac{d^{m+1}}{dx^{m+1}}P_l+\frac{d^2}{dx^2}\left(\sqrt{1-x^2}\right)^m\left(1-x^2\right)\frac{d^m}{dx^m}P_l$$

$$=: A_1+A_2+A_3$$

$$A_3:=\left(\sqrt{1-x^2}\right)^m\left(1-x^2\right)\frac{d^{m+2}}{dx^{m+2}}P_l=\left(\sqrt{1-x^2}\right)^m\left(\frac{d^m}{dx^m}\left(\left(1-x^2\right)\frac{d^2}{dx^2}P_l\right)+2mx\frac{d^{m+1}}{dx^{m+1}}P_l+m\left(m-1\right)\frac{d^m}{dx^m}P_l\right)=: A_4+A_5+A_6$$

- And $B$ is:

$$-2x\frac{d}{dx}\left(\left(\sqrt{1-x^2}\right)^m\frac{d^m}{dx^m}P_l\right)=-2x\frac{d}{dx}\left(\sqrt{1-x^2}\right)^m\frac{d^m}{dx^m}P_l-2x\left(\sqrt{1-x^2}\right)^m\frac{d^{m+1}}{dx^{m+1}}P_l=: B_1+B_2$$

$$-2x\left(\sqrt{1-x^2}\right)^m\frac{d^{m+1}}{dx^{m+1}}P_l=\left(\sqrt{1-x^2}\right)^m\left(\frac{d^m}{dx^m}\left(-2x\frac{dP_l}{dx}\right)+2m\frac{d^m}{dx^m}P_l\right)=: B_3+B_4$$

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# Associated Legendre Functions

- $C$ is:

$$-l\left(l+1\right)\left(\sqrt{1-x^2}\right)^m \frac{\mathrm{d}^m}{\mathrm{d}x^m}\mathrm{P}_l$$

- We note that $A_4$, $B_3$, $C$ are components of the Legendre equation($m$=0) LHS, so their sum vanishes.
- Collect the residues and categorize them by the orders of derivative:

$$\left(\left(\sqrt{1-x^2}\right)^m 2mx+\frac{\mathrm{d}}{\mathrm{d}x}\left(\sqrt{1-x^2}\right)^m 2\left(1-x^2\right)\right)\frac{\mathrm{d}^{m+1}}{\mathrm{d}x^{m+1}}\mathrm{P}_l+\left(\sqrt{1-x^2}\right)^m\left(2m+m\left(m-1\right)-2x\frac{\mathrm{d}}{\mathrm{d}x}\left(\sqrt{1-x^2}\right)^m+\frac{\mathrm{d}^2}{\mathrm{d}x^2}\left(\sqrt{1-x^2}\right)^m\left(1-x^2\right)\right)\frac{\mathrm{d}^m}{\mathrm{d}x^m}\mathrm{P}_l$$

- Due to that:

$$\frac{\mathrm{d}}{\mathrm{d}x}\left(\sqrt{1-x^2}\right)^m=\frac{-mx}{1-x^2}\left(\sqrt{1-x^2}\right)^m$$

- The $m$+1 order derivative vanishes.

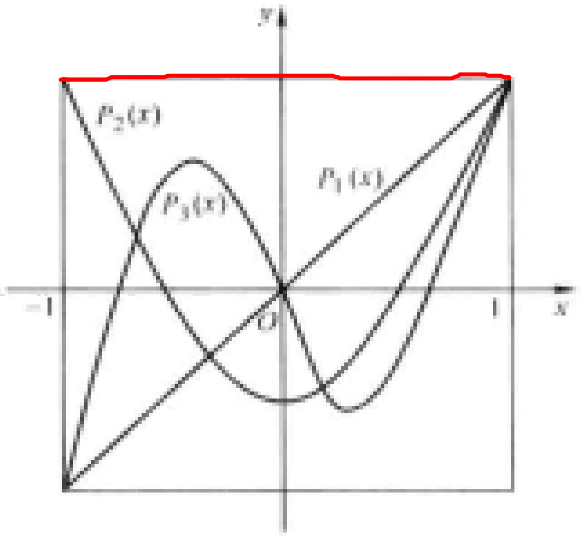
# Associated Legendre Functions

- After you calculate the 2-order-derivative of $(1-x^2)^{m/2}$, you can verify that the result is:

$$\frac{m^2}{1-x^2}\left(\sqrt{1-x^2}\right)^m \frac{\mathrm{d}^m}{\mathrm{d}x^m}\mathrm{P}_l =: \frac{m^2}{1-x^2}\mathrm{P}_l^m$$

- Which means that $P_l^m$, the ALF, with two indices, is the solution of Legendre equation having the corresponding *l* and *m*.

# Properties of LPs and ALFs




- $l$ order LPs have $l$ zeroes.
- Even-order LPs are even functions, vice versa.
- ALFs have $l-m$ zeroes, this can be easily imagined as ALF contains components of $m$-order derivatives.

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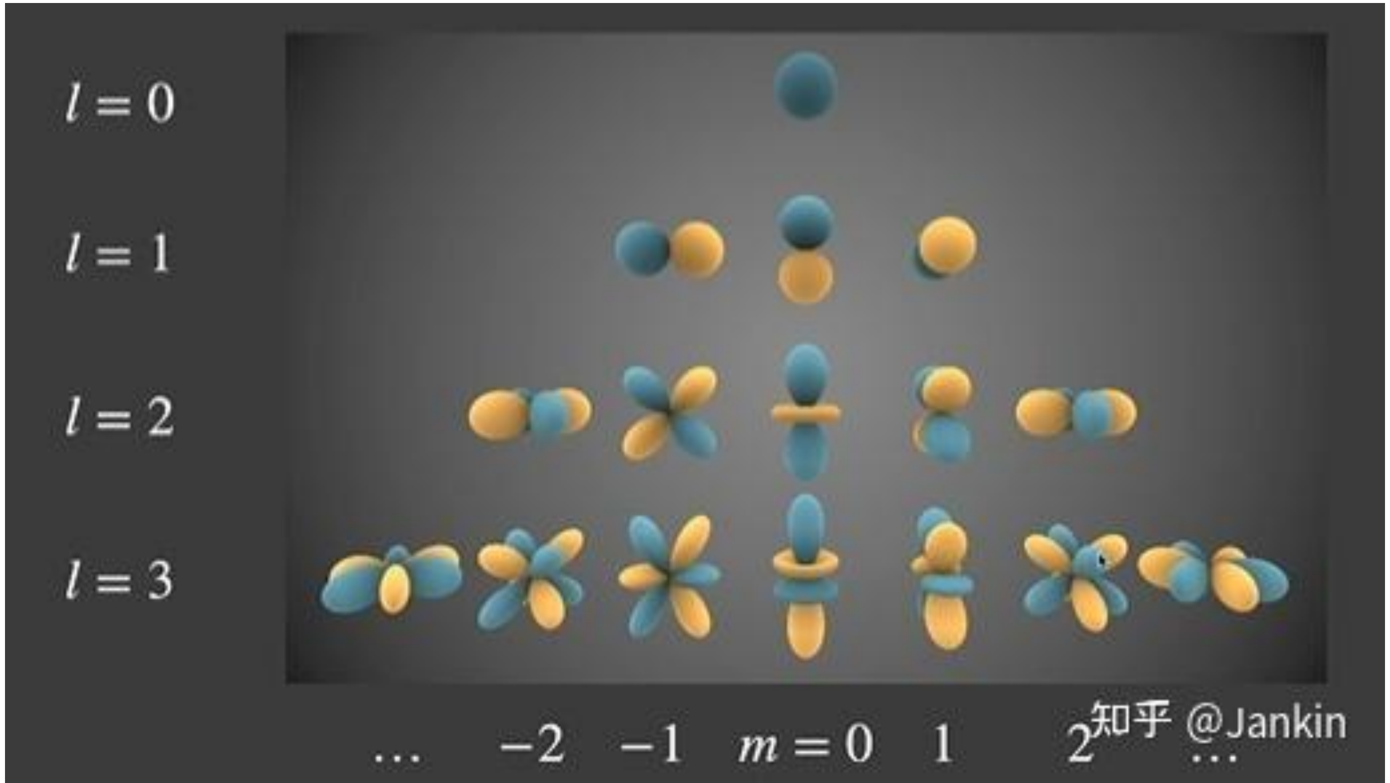
# Spherical Harmonics

- We combine the Θ and Φ functions, and we can define a spherical harmonic:

$$Y_l^m(\theta,\phi) = P_l^m(\cos\theta)\mathrm{e}^{im\phi}$$



# To be continued…

- Radial Equation of Hydrogen Atom
- Zeroes' theorem of Sturm-Liouville systems