

# 工程数学

Engineering Mathematics

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## ① 氢原子薛定谔方程分离变量

相对坐标系

球坐标拉普拉斯

球坐标氢原子方程

## ② 角向方程与勒让德多项式

经/纬度分离

勒让德多项式

连带勒让德多项式

## ③ 径向方程与拉盖尔多项式

广义拉盖方程

拉盖方程多项式

广义拉盖方程多项式

# 第四章 氢原子

## (6 学时)

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# 氢原子薛定谔方程

氢原子含一原子核和一核外电子，是二体问题。

哈密顿量为：

$$H = \left[ -\frac{\hbar^2}{2m_1} \nabla_1^2 + V(\vec{r}_1, t) \right] + \left[ -\frac{\hbar^2}{2m_2} \nabla_2^2 + V(\vec{r}_2, t) \right] + U(|\vec{r}_1 - \vec{r}_2|)$$

其中  $V$  为， $U$  为库仑势：

$$U(|\vec{r}_1 - \vec{r}_2|) = -\frac{e_s^2}{|\vec{r}_1 - \vec{r}_2|} \quad , \quad e_s = \frac{Ze}{\sqrt{4\pi\epsilon_0}}$$

薛定谔方程为:

$$i\hbar \frac{\partial}{\partial t} \Psi(\vec{r}_1, \vec{r}_2, t) = H(\vec{r}_1, \vec{r}_2, t) \Psi(\vec{r}_1, \vec{r}_2, t)$$

当背景势  $V$  不显含时间  $t$ , 时空可分离变量。解得时间函数:

$$f(t) = e^{-iEt/\hbar}$$

空间函数服从定态薛定谔方程:

$$\left[ -\frac{\hbar^2}{2m_1} \nabla_1^2 + V_1 - \frac{\hbar^2}{2m_2} \nabla_2^2 + V_2 + U_{1,2} \right] \Psi(\vec{r}_1, \vec{r}_2) = E \Psi(\vec{r}_1, \vec{r}_2)$$

# 相对坐标

设背景势  $V=0$ ，简化为：

$$\left[ -\frac{\hbar^2}{2m_1} \nabla_1^2 - \frac{\hbar^2}{2m_2} \nabla_2^2 + U(|\vec{r}_1 - \vec{r}_2|) \right] \Psi(\vec{r}_1, \vec{r}_2) = E \Psi(\vec{r}_1, \vec{r}_2)$$

引入相对坐标和质心坐标，令：

$$\begin{cases} \vec{r}(x, y, z) = \vec{r}_1 - \vec{r}_2 \\ \vec{R}(X, Y, Z) = \frac{m_1 \vec{r}_1 + m_2 \vec{r}_2}{m_1 + m_2} \\ \begin{cases} M = m_1 + m_2 \\ m = \frac{m_1 m_2}{m_1 + m_2} \end{cases} \end{cases}$$

对坐标函数:  $\begin{cases} \vec{r}_1 = f_1(\vec{r}, \vec{R}) \\ \vec{r}_2 = f_2(\vec{r}, \vec{R}) \end{cases}$

求导:

$$\frac{d}{dx_1} = \frac{\partial}{\partial X} \frac{\partial X}{\partial x_1} + \frac{\partial}{\partial x} \frac{\partial x}{\partial x_1} = \frac{m_1}{M} \frac{\partial}{\partial X} + \frac{\partial}{\partial x}$$

$$\frac{d^2}{dx_1^2} = \frac{m_1^2}{M^2} \frac{\partial^2}{\partial X^2} + \frac{2m_1}{M} \frac{\partial^2}{\partial X \partial x} + \frac{\partial^2}{\partial x^2}$$

$$\nabla_1^2 = \frac{m_1^2}{M^2} \nabla_R^2 + \frac{2m_1}{M} \left( \frac{\partial^2}{\partial X \partial x} + \frac{\partial^2}{\partial Y \partial y} + \frac{\partial^2}{\partial Z \partial z} \right) + \nabla^2$$

$$\nabla_2^2 = \frac{m_2^2}{M^2} \nabla_R^2 - \frac{2m_2}{M} \left( \frac{\partial^2}{\partial X \partial x} + \frac{\partial^2}{\partial Y \partial y} + \frac{\partial^2}{\partial Z \partial z} \right) + \nabla^2$$



结合在一起，得：

$$\frac{1}{m_1} \nabla_1^2 + \frac{1}{m_2} \nabla_2^2 = \frac{1}{M} \nabla_R^2 + \frac{1}{m} \nabla^2$$

代回简化后的方程，得：

$$\left[ -\frac{\hbar^2}{2M} \nabla_R^2 - \frac{\hbar^2}{2m} \nabla^2 + U(\vec{r}) \right] \Psi(\vec{R}, \vec{r}) = E \Psi(\vec{R}, \vec{r})$$

相对和质心坐标可分离变量，

令：  $\Psi(\vec{R}, \vec{r}) = \psi(\vec{R})\Psi(\vec{r})$ , 代入上方程，得方程 (1)：

$$-\frac{\hbar^2}{2M}\nabla_{\vec{R}}^2\psi(\vec{R}) = E_c\psi(\vec{R}).....(1)$$

这是二体的质心运动方程，解为自由粒子平面波：

$$\psi(\vec{R}, t) = -\frac{1}{(2\pi\hbar)^{3/2}}e^{-\frac{i}{\hbar}(E_c t - \vec{p} \cdot \vec{R})}$$

方程 (2)：

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

这是二体相对运动方程，核与核外电子相对质心的运动方程。是核外电子相对于核的运动方程的近似！

U 为库仑势:

$$U(\vec{r}) = -\frac{e_s^2}{r} \quad , \quad r = \sqrt{x^2 + y^2 + z^2}$$

与角量无关。方程 (2) 应改用球坐标系描述。

$$\left[ -\frac{\hbar^2}{2\mu} \nabla^2 + U(r) \right] \Psi(\vec{r}) = E \Psi(\vec{r}) \dots (2)$$

问题的关键在如何把  $(x, y, z)$  的  $\nabla^2$  用  $(r, \theta, \varphi)$  坐标系进行描述

# 球坐标拉普拉斯算子

已知  $(x, y, z)$  坐标系下的拉普拉斯算子为

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

求  $(r, \theta, \varphi)$  坐标系下的拉普拉斯算子

**解:** 坐标的变换关系为:

$$\begin{cases} x = r \sin \theta \cos \varphi \\ y = r \sin \theta \sin \varphi \\ z = r \cos \theta \end{cases}$$

对函数  $u(x, y, z)$ , 进行  $r, \theta, \varphi$  求导, 有:

$$\begin{cases} \frac{\partial u}{\partial r} = \frac{\partial u}{\partial x} \frac{\partial x}{\partial r} + \frac{\partial u}{\partial y} \frac{\partial y}{\partial r} + \frac{\partial u}{\partial z} \frac{\partial z}{\partial r} \\ \frac{\partial u}{\partial \theta} = \frac{\partial u}{\partial x} \frac{\partial x}{\partial \theta} + \frac{\partial u}{\partial y} \frac{\partial y}{\partial \theta} + \frac{\partial u}{\partial z} \frac{\partial z}{\partial \theta} \\ \frac{\partial u}{\partial \varphi} = \frac{\partial u}{\partial x} \frac{\partial x}{\partial \varphi} + \frac{\partial u}{\partial y} \frac{\partial y}{\partial \varphi} + \frac{\partial u}{\partial z} \frac{\partial z}{\partial \varphi} \end{cases}$$

$$\begin{bmatrix} \frac{\partial u}{\partial r} \\ \frac{\partial u}{\partial \theta} \\ \frac{\partial u}{\partial \varphi} \end{bmatrix} = \begin{bmatrix} \sin \theta \cos \varphi & \sin \theta \sin \varphi & \cos \theta \\ r \cos \theta \cos \varphi & r \cos \theta \sin \varphi & -r \sin \theta \\ -r \sin \theta \sin \varphi & r \sin \theta \cos \varphi & 0 \end{bmatrix} \begin{bmatrix} \frac{\partial u}{\partial x} \\ \frac{\partial u}{\partial y} \\ \frac{\partial u}{\partial z} \end{bmatrix}$$

$$\begin{bmatrix} \frac{\partial u}{\partial r} \\ \frac{\partial u}{\partial \theta} \\ \frac{\partial u}{\partial \varphi} \end{bmatrix} = \begin{bmatrix} \sin \theta \cos \varphi & \sin \theta \sin \varphi & \cos \theta \\ \cos \theta \cos \varphi & \cos \theta \sin \varphi & -\sin \theta \\ -\sin \varphi & \cos \varphi & 0 \end{bmatrix} \begin{bmatrix} \frac{\partial u}{\partial x} \\ \frac{1}{r} \frac{\partial u}{\partial y} \\ \frac{1}{r \sin \theta} \frac{\partial u}{\partial z} \end{bmatrix}$$

$$\begin{bmatrix} \frac{\partial u}{\partial r} \\ \frac{\partial u}{\partial \theta} \\ \frac{\partial u}{\partial \varphi} \end{bmatrix} = \begin{bmatrix} e_r & e_\theta & e_\varphi \end{bmatrix} \begin{bmatrix} \frac{\partial u}{\partial x} \\ \frac{1}{r} \frac{\partial u}{\partial y} \\ \frac{1}{r \sin \theta} \frac{\partial u}{\partial z} \end{bmatrix}$$

$$\rightarrow \nabla = e_r \frac{\partial}{\partial r} + \frac{1}{r} e_\theta \frac{\partial}{\partial \theta} + \frac{1}{r \sin \theta} e_\varphi \frac{\partial}{\partial \varphi}$$

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

$$\begin{aligned}
 &= \left( e_r \frac{\partial}{\partial r} + \frac{1}{r} e_\theta \frac{\partial}{\partial \theta} + \frac{1}{r \sin \theta} e_\varphi \frac{\partial}{\partial \varphi} \right) \cdot \left( e_r \frac{\partial}{\partial r} + \frac{1}{r} e_\theta \frac{\partial}{\partial \theta} + \frac{1}{r \sin \theta} e_\varphi \frac{\partial}{\partial \varphi} \right) \\
 &= \frac{\partial^2}{\partial r^2} + \left( \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} \right) + \left( \frac{1}{r} \frac{\partial}{\partial r} + \frac{\cos \theta}{r^2 \sin \theta} \frac{\partial}{\partial \theta} + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right) \\
 &= \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \varphi^2}
 \end{aligned}$$

tips: 利用单位矢的正交归一性和微分性质进行计算 (见讲义 15 页)

直角坐标  $(x, y, z)$ :

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

球坐标  $(r, \theta, \varphi)$  :

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

令角向部分为:

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

有:

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial}{\partial r}) - \frac{1}{r^2} L^2$$



# 角向算符与角动量算符

角向算子:

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

角动量算子:

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

角动量的径向和切向分量

$$p_r^2 = -\hbar^2 \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial}{\partial r}), \quad p_{\perp}^2 = \frac{L^2}{r^2}$$

# 求角动量算符

$$\begin{cases} x = r \sin \theta \cos \varphi \\ y = r \sin \theta \sin \varphi \\ z = r \cos \theta \end{cases}$$

矩阵形式:

$$\begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} r \sin \theta \cos \varphi \\ r \sin \theta \sin \varphi \\ r \cos \theta \end{bmatrix} = r e_r$$

动量算子:

$$\hat{p} = -i\hbar \nabla = -i\hbar \left( e_r \frac{\partial}{\partial r} + \frac{1}{r} e_\theta \frac{\partial}{\partial \theta} + \frac{1}{r \sin \theta} e_\varphi \frac{\partial}{\partial \varphi} \right)$$

角动量:  $\vec{L} = \vec{r} \times \vec{p}$

算子为:

$$\hat{L} = \hat{r} \times \hat{p} = -i\hbar r e_r \times \nabla$$

$$\hat{L} = -i\hbar \left( e_\varphi \frac{\partial}{\partial \theta} - \frac{1}{\sin \theta} e_\theta \frac{\partial}{\partial \varphi} \right)$$

角动量的 Z 分量:

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \varphi}$$

$$\hat{L}^2 = -\hbar^2 \left( e_\varphi \frac{\partial}{\partial \theta} - \frac{1}{\sin \theta} e_\theta \frac{\partial}{\partial \varphi} \right) \cdot \left( e_\varphi \frac{\partial}{\partial \theta} - \frac{1}{\sin \theta} e_\theta \frac{\partial}{\partial \varphi} \right)$$

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

# 球坐标氢原子方程

球坐标下的哈密顿量（折合质量  $m$  计为  $\mu$ ）:

$$H = -\frac{\hbar^2}{2\mu r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial}{\partial r}) + \frac{\hbar^2}{2\mu r^2} L^2 - \frac{e_s^2}{r} = \frac{1}{2\mu} p_r^2 + \frac{1}{2\mu r^2} L^2 - \frac{e_s^2}{r}$$

球坐标氢原子定态方程:

$$\left[ \frac{1}{2\mu} p_r^2 + \frac{1}{2\mu} p_{\perp}^2 - \frac{e_s^2}{r} \right] \Psi(r, \theta, \varphi) = E \Psi(r, \theta, \varphi)$$

方程可做动量的径向/切向分离.....

为了与数学方程统一，采用角向算符  $L^2$ （与角动量算符差一个  $\hbar^2$ ）：

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

球坐标系下的方程形式变为：

$$\left[ -\frac{\hbar^2}{2\mu r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial}{\partial r}) - \frac{\hbar^2}{2\mu r^2} L^2 - \frac{e_s^2}{r} \right] \Psi = E \Psi$$

数学上的径向/角向分离，令：

$$\Psi = R(r)Y(\theta, \varphi)$$

代回原方程，得：

$$-\frac{L^2 Y}{Y} = \frac{1}{R} \frac{\partial}{\partial r} (r^2 \frac{\partial R}{\partial r}) + \frac{2\mu r^2}{\hbar^2} (E + \frac{e_s^2}{r}) = \lambda$$

氢原子的空间方程在球坐标系下分离成两个方程：

(1) 角向方程：

$$L^2 Y = -\lambda Y$$

(2) 径向方程：

$$\frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{2\mu r^2}{\hbar^2} \left( E + \frac{e_s^2}{r} \right) R = \lambda R$$

分别求解径向/角向方程...

# 作业

- 1、求基向量  $(e_r, e_\theta, e_\varphi)$  点积和叉积的运算规律
- 2、求如下偏分

$$\frac{\partial}{\partial \theta} e_\theta, \quad \frac{\partial}{\partial \theta} e_r$$

- 3、角向算子与角动量算子有什么区别？

## 球坐标氢原子方程

## 连带勒让德多项式

# 广义拉盖方程多项式



# 经纬度分离变量

角向方程:

$$L^2 Y = -\lambda Y \rightarrow L^2 Y = -l(l+1)Y$$

代入角向算子:

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

可进一步进行经/纬度变量分离, 令:

$$Y(\theta, \varphi) = \Theta(\theta)\Phi(\varphi)$$

代回上方程。得:

$$\Phi \frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + \Theta \frac{1}{\sin^2 \theta} \frac{d^2 \Phi}{d\varphi^2} + l(l+1)\Theta\Phi = 0$$

整理得：

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

分离变量，得（1）经度方程：

$$\frac{d^2 \Phi}{d\varphi^2} + \lambda \Phi = 0, (0 < \varphi < 2\pi)$$

（2）纬度方程：

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

# 解经度方程

经度方程是周期性边界条件固有值问题:

$$\frac{d^2\Phi}{d\varphi^2} + \lambda\Phi = 0, 0 < \varphi < 2\pi$$

$$\Phi(0) = \Phi(2\pi), \Phi'(0) = \Phi'(2\pi)$$

特征方程有两虚根, 对应固有值和固有函数为:

$$\lambda = m^2, \quad (m = 0, 1, 2, \dots)$$

$$\Phi(\varphi) = A \cos m\varphi + B \sin m\varphi$$

写在指数形式

$$\Phi_m(\varphi) = A_m e^{im\varphi}$$

求归一化系数:

$$\int_0^{2\pi} |\Phi_m(\varphi)|^2 d\varphi = 1$$

$$\int_0^{2\pi} A_m e^{im\varphi} A_m e^{-im\varphi} d\varphi = 1$$

$$A_m^2 \int_0^{2\pi} 1 d\varphi = 1$$

$$A_m^2 2\pi = 1$$

$$A_m = \frac{1}{\sqrt{2\pi}}$$

$$\Phi_m(\varphi) = \frac{1}{\sqrt{2\pi}} e^{im\varphi}$$

## 解纬度方程

把固有值代回纬度方程, 得  $n$  阶连带勒让德方程:

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

**解:**微分展开, 再整理, 得:

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

令:  $x = \cos \theta$ ,  $y(x) = y(\cos \theta) = \Theta(\theta)$ , 有, 做微分计算:

$$\frac{dx}{d\theta} = -\sin \theta$$

$$\frac{d\Theta}{d\theta} = \frac{dy}{dx} \frac{dx}{d\theta} = -\sin \theta \frac{dy}{dx}$$

$$\frac{d^2\Theta}{d\theta^2} = -\sin^2\theta \frac{d^2y}{dx^2} - \cos\theta \frac{dy}{dx}$$

代回方程（注意  $\cos\theta = x$ ,  $\sin\theta = 1 - x^2$ ），  
得标准连带勒让德方程：

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

令  $m=0$ ，得勒让德方程：

$$(1-x^2) \frac{d^2y}{dx^2} - 2x \frac{dy}{dx} + l(l+1)y = 0$$

# 解勒让德方程

$$(1 - x^2) \frac{d^2 y}{dx^2} - 2x \frac{dy}{dx} + l(l + 1)y = 0$$

**解:** 令方程有级数解,

$$y = \sum_{k=0}^{\infty} a_k x^k$$

求导, 并代回上方向, 得:

$$\sum_{k=0}^{\infty} \{(k + 1)(k + 2)a_{k+2} + [l(l + 1) - k(k + 1)]a_k\} x^k = 0$$

系数项为零:

$$(k + 1)(k + 2)a_{k+2} + [l(l + 1) - k(k + 1)]a_k = 0$$

得递推式:

$$a_{k+2} = -\frac{l(l+1) - k(k+1)}{(k+1)(k+2)} a_k$$

k 为偶数:

$$y_1(x) = a_0 \left[ 1 - \frac{l(l+1)}{2} x^2 + \frac{l(l+1)(l+3)(l-2)}{4!} x^4 + \dots \right]$$

k 为奇数:

$$y_2(x) = a_1 \left[ x - \frac{(l-1)(l+2)}{3!} x^3 + \frac{(l+2)(l+3)(l-1)(l-3)}{5!} x^5 + \dots \right]$$

方程的级数解:

$$y(x) = y_1(x) + y_2(x)$$



# 勒让德多项式

逆向递推式为 ( $l=n$ ):

$$a_{k-2} = -\frac{(k-1)k}{(n-k+2)(n+k-1)}a_k$$

注意到级数解应只含有限多项，取最高项  $k=n$

$$a_{n-2} = -\frac{(n-1)n}{2(2n-1)}a_n$$

令最高项系数:

$$a_n = \frac{(2n)!}{2^n(n!)^2}$$

有:

$$a_{n-2} = -\frac{(2n-2)!}{2^n(n-1)!(n-2)!}$$

一般式:

$$a_{n-2m} = (-1)^m \frac{(2n-2m)!}{2^n m! (n-m)! (n-2m)!}$$

得勒让德方程的多项式解:

$$P_n(x) = \sum_{m=0}^{[n/2]} (-1)^m \frac{(2n-2m)!}{2^n m! (n-m)! (n-2m)!} x^{n-2m}$$

称为勒让德多项式。

取  $x = \cos \theta$ , 得球谐函数, 见下表:

$P_0(x) = 1$	
$P_1(x) = x$	$P_1(\cos \theta) = \cos \theta$
$P_2(x) = \frac{1}{2}(3x^2 - 1)$	$P_2(\cos \theta) = \frac{1}{4}[3 \cos 2\theta + 1]$
$P_3(x) = \frac{1}{2}(5x^3 - 3x)$	$P_3(\cos \theta) = \frac{1}{8}[5 \cos 3\theta + 3 \cos \theta]$
$P_4(x) = \frac{1}{8}(35x^4 - 30x^2 + 3)$	$P_4(\cos \theta) = \frac{1}{64}[35 \cos 4\theta + 20 \cos 2\theta + 9]$

**性质 1:** 勒让德多项式具有如下微分形式:

$$P_n(x) = \frac{1}{2^n n!} \frac{d^n}{dx^n} (x^2 - 1)^n, \quad (n = 0, 1, 2, 3, \dots)$$

**证明:** 由二项式定理, 有:

$$(x^2 - 1)^n = \sum_{m=0}^n C_n^m (-1)^m (x^2)^{n-m} = \sum_{m=0}^n \frac{(-1)^m n!}{m!(n-m)!} x^{2n-2m}$$

求  $n$  次导,

$$\frac{d^n}{dx^n} (x^2 - 1)^n = \sum_{m=0}^n \frac{(-1)^m n!}{m!(n-m)!} \frac{d^n}{dx^n} (x^{2n-2m})$$

当  $2n - 2m < n$  时，上次的右边导数为零，即非零的最高项为  $[n/2]$ ，有：

$$\frac{d^n}{dx^n} (x^2 - 1)^n = \sum_{m=0}^{[n/2]} \frac{(-1)^m n!}{m!(n-m)!} \frac{d^n}{dx^n} (x^{2n-2m})$$

$$\frac{1}{2^n n!} \frac{d^n}{dx^n} (x^2 - 1)^n = \frac{1}{2^n n!} \sum_{m=0}^{[n/2]} \frac{(-1)^m n!}{m!(n-m)!} \frac{d^n}{dx^n} (x^{2n-2m}) = P_n(x)$$

证毕！

**性质 2:**勒让德多项式具有如下母函数:

$$w(x, z) = (1 - 2zx + z^2)^{-1/2}$$

**证明:**即要证

$$(1 - 2zx + z^2)^{-1/2} = \sum_{n=0}^{\infty} P_n(x)z^n$$

由二项式定理有:

$$(1 + v)^p = \sum_{k=0}^{\infty} \frac{p(p-1) \cdots (p-k+1)}{k!} v^k$$

取  $p = -1/2$ , 得:

$$(1 + v)^{-1/2} = \sum_{k=0}^{\infty} (-1)^k \frac{(2k)!}{2^{2k}(k!)^2} v^k$$

取  $v = -2zx + z^2 = -z(2x - z)$ , 有:

$$v^k = (-1)^k z^k (2x - z)^k = (-1)^k z^k \sum_{m=0}^k C_k^m (2x)^{k-m} (-z)^m$$

代回上式, 得:

$$(1 - 2zx + z^2)^{-\frac{1}{2}} = \sum_{k=0}^{\infty} \frac{(2k)!}{2^{2k}(k!)^2} \sum_{m=0}^k (-1)^m C_k^m (2x)^{k-m} z^{k+m}$$

令:  $k - m = n$ , 即要证明上式右边的系数就是  $P_n(x)$ !

$$\sum_{k+m=n} 2^{2k} (k!)^2 (-1)^m C_k^m (2x)^{k-m}$$

$$= \sum_{m=0}^n (-1)^m \frac{(2n-2m)!}{2^{2(n-m)} (n-m)! m! (n-2m)!} \frac{1}{(2x)^{n-2m}}$$

$$= \sum_{m=0}^n (-1)^m \frac{(2n-2m)!}{2^n m! (n-m)! (n-2m)!} x^{n-2m}$$

$$= P_n(x)$$

证毕!



**性质 3:** 勒让德多项式具有如下递推关系:

$$(n+1)P_{n+1}(x) - (2n+1)xP_n(x) + nP_{n-1}(x) = 0$$

**证明:** 对于母函数的形式级数:

$$w(x, z) = (1 - 2zx + z^2)^{-1/2} = \sum_{n=0}^{\infty} P_n(x)z^n$$

求关于  $z$  的偏导:

$$\frac{\partial w}{\partial z} = \sum_{n=1}^{\infty} nP_n(x)z^{n-1} = \sum_{n=0}^{\infty} (n+1)P_{n+1}(x)z^n$$

$$\frac{\partial w}{\partial z} = (x - z)(1 - 2zx + z^2) - 3/2$$

$$(1 - 2zx + z^2) \frac{\partial w}{\partial z} = (x - z)(1 - 2zx + z^2) - 1/2$$

$$(1 - 2zx + z^2) \frac{\partial w}{\partial z} - (x - z)w = 0$$

$$(1 - 2zx + z^2) \sum_{n=0}^{\infty} (n+1)P_{n+1}z^n - (x - z) \sum_{n=0}^{\infty} P_n(x)z^n = 0$$

整理，得

$$\sum_{n=1}^{\infty} [(n+1)P_{n+1} - (2n+1)xP_n + nP_{n-1}]z^n = 0$$

系数项等于零，**得证！**

**性质 4:** 勒让德多项式具有正交性:

**证明:** 勒让德多项式满足勒让德方程

$$(1-x^2)P_n''(x) - 2xP_n'(x) + n(n+1)P_n(x) = 0$$

等价形式:

$$[(1-x^2)P_n'(x)]' + n(n+1)P_n(x) = 0 \cdots (1)$$

同理:

$$(1-x^2)P_m'(x)' + m(m+1)P_m(x) = 0 \cdots (2)$$

(1) 式  $\times P_m$ , (2) 式  $\times P_n$ , 所得两式相减并积分:

$$[n(n+1)-m(m+1)] \int_{-1}^1 P_m P_n dx = \int_{-1}^1 (P_m [(1-x^2)P_n']' - P_n [(1-x^2)P_m']') dx$$

上式右端分部积分,

$$\begin{aligned}
 &= (P_m[(1-x^2)P'_n] - P_n[(1-x^2)P'_m])|_{-1}^1 \\
 &\quad - \int_{-1}^1 [(1-x^2)P'_mP'_n - (1-x^2)P'_nP'_m]dx \\
 &= 0
 \end{aligned}$$

因此,

$$[n(n+1) - m(m+1)] \int_{-1}^1 P_m P_n dx = 0$$

有:

$$\int_{-1}^1 P_m P_n dx = 0, \dots (n \neq m)$$

证毕!

## 性质 5: 勒让德多项式具有归一性

$$\int_{-1}^1 P_n P_n dx = \frac{2}{2n+1}$$

## 证明: 有递推公式

$$[nP_n - (2n-1)xP_{n-1} + (n-1)P_{n-2}] = 0$$

$$nP_n^2 = (2n-1)xP_n P_{n-1} - (n-1)P_n P_{n-2}$$

$$\int_{-1}^1 nP_n^2 dx = \int_{-1}^1 (2n-1)xP_n P_{n-1} dx$$

递推式写成  $xP_n = AP_{n+1} + BP_{n-1}$  代入上式, 得积分递推式

$$\int_{-1}^1 P_n^2 dx = \frac{2n-1}{2n+1} \int_{-1}^1 P_{n-1}^2 dx$$

反复递推：

$$\int_{-1}^1 P_n^2 dx = \frac{1}{2n+1} \int_{-1}^1 P_0^2 dx = \frac{2}{2n+1}$$

证毕！

# 连带勒让德多项式

勒让德方程：

$$(1-x^2)\frac{d^2y}{dx^2} - 2x\frac{dy}{dx} + l(l+1)y = 0$$

解为勒让德多项式

$$P_n(x) = \frac{1}{2^n n!} \frac{d^n}{dx^n} (x^2-1)^n, \quad (n=0,1,2,3,\dots)$$

同理可解连带勒让德方程：

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

解为连带勒让德多项式

$$P_n^m(x) = (1-x^2)^{m/2} \frac{d^m}{dx^m} P_n(x), \quad (m \leq n, n=1,2,3,\dots)$$

## 连带勒让德多项式性质:

(1) 正交性:

$$\int_{-1}^1 P_m^k P_n^k dx = 0, \cdots (n \neq m)$$

(2) 归一性:

$$\int_{-1}^1 P_n^k P_n^k dx = \frac{(n+k)!}{(n-k)!} \frac{2}{2n+1}$$

(3) 递推式:

$$(n+1-k)P_{n+1}^k - (2n+1)xP_n^k + (n+k)P_{n-1}^k = 0$$



# 球谐函数

氢原子角向方程：

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

其解为球谐函数：

$$Y(\theta, \varphi) = \Theta(\theta)\Phi(\varphi)$$

经度解函数为：

$$\Phi_m(\varphi) = \frac{1}{\sqrt{2\pi}} e^{im\varphi}$$

纬度解函数为：

$$\Theta(\theta) = P_n^m(\cos \theta), \quad (m \leq n, n = 1, 2, 3, \dots \dots)$$

# 角向函数归一化

$$Y_{lm}(\theta, \varphi) = A_{lm} P_l^m(\cos\theta) e^{im\varphi}$$

求归一化系数

$$\iint |Y_{lm}|^2 d\sigma = 1$$

$$\iint A_{lm}^2 |P_l^m(\cos\theta)|^2 |\Phi(\varphi)|^2 d\sigma = 1$$

$$A_{lm}^2 2\pi \int_0^\pi |P_l^m(\cos\theta)|^2 \sin\theta d\theta = 1$$

$$A_{lm}^2 2\pi \frac{(l+m)!}{(l-m)!} \frac{2}{2l+1} = 1$$

$$A_{lm} = \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}}$$

# 作业

- 1、将  $x = \cos \theta$  代入勒让德多项式, 写出前 4 个勒让德多项式表达式
- 2、计算积分

$$\int_{-1}^1 P_1(x)P_2(x)dx, \quad \int_{-1}^1 P_2(x)P_2(x)dx$$

# ① 氢原子薛定谔方程分离变量

相对坐标系

球坐标拉普拉斯

球坐标氢原子方程

# ② 角向方程与勒让德多项式

经/纬度分离

勒让德多项式

连带勒让德多项式

# ③ 径向方程与拉盖尔多项式

广义拉盖方程

拉盖方程多项式

广义拉盖方程多项式

# 径向方程与广义拉盖方程

径向方程:

$$\frac{d}{dr}(r^2 \frac{dR}{dr}) + \frac{2\mu r^2}{\hbar^2}(E + \frac{e_s^2}{r}) = \lambda R$$

解: 取  $\lambda = l(l+1)$

$$\frac{d}{dr}(r^2 \frac{dR}{dr}) + \frac{2\mu r^2}{\hbar^2}(E + \frac{e_s^2}{r})R = l(l+1)R$$

$$\frac{d^2 R}{dr^2} + \frac{2}{r^2} \frac{dR}{dr} + \frac{2\mu}{\hbar^2}(E + \frac{e_s^2}{r})R - \frac{l(l+1)}{r^2}R = 0$$

令  $\xi = \alpha r$ ,  $U(\xi) = R(\xi/\alpha)$ ,  $\alpha = \sqrt{-\frac{8\mu E}{\hbar^2}}$ ,  $\beta = \frac{2\mu e_s^2}{\alpha \hbar^2}$ ,

进行伸缩变换....., 得:

$$\frac{d^2 U}{d\xi^2} + \frac{2}{\xi} \frac{dU}{d\xi} - [\frac{1}{4} - \frac{\beta}{\xi} + \frac{l(l+1)}{\xi^2}]U = 0 \dots (1)$$

考虑方程解的渐近行为:

(1)  $r \rightarrow \infty, \xi \rightarrow \infty$ , 有方程:

$$\frac{d^2 U}{d\xi^2} - \frac{1}{4}U = 0$$

特征方程有两互异实根, 通解为:

$$U = C_1 \exp\left(\frac{1}{2}\xi\right) + C_2 \exp\left(-\frac{1}{2}\xi\right)$$

考虑到有界性, 有特解:

$$U_\infty = C \exp\left(-\frac{1}{2}\xi\right)$$

(2)  $r \rightarrow 0, \xi \rightarrow 0$ , 有欧拉方程:

$$\frac{d^2 U}{d\xi^2} + \frac{2}{\xi} \frac{dU}{d\xi} + \left[ \frac{\beta}{\xi} - \frac{l(l+1)}{\xi^2} \right] U = 0$$

通解为:

$$U = C_1 \xi^{-(l+1)} + C_2 \xi^l$$

考虑到有界性, 有特解:

$$U_0 = C \xi^l$$

作常数变异, 令方程的解为:

$$U = H(\xi) \xi^l \exp\left(-\frac{1}{2}\xi\right)$$

问题变为求多项式  $H(\xi)$

对上次求导，并把结果代回原方程 (1)，得

$$\xi H'' + [2(l+1) - \xi]H' - [\beta - (l+1)]H = 0$$

标准的广义拉盖方程为

$$xH'' + [m+1-x]H' + nH = 0$$

对比以上两方程，发现当

$$m = 2l + 1, \quad n = -\beta + (l+1)$$

时，方程正是广义拉盖方程，问题转化为求广义拉盖方程



# 解拉盖方程

取  $m = 0$ , 得一般的拉盖方程, 取标准形式:

$$xy'' + [1 - x]y' + ny = 0$$

**解:** 设方程有级数解

$$y = \sum_{k=0}^{\infty} c_k x^k$$

求导, 代回上方程, 得

$$\sum_{k=0}^{\infty} [(n - k)c_k + (k + 1)^2 c_{k+1}] x^k = 0$$

得系数递推式:

$$c_{k+1} = -\frac{n - k}{(k + 1)^2} c_k, \quad (k = 0, 1, 2, \dots)$$

反复递推，有：

$$c_k = (-1)^k \frac{n(n-1) \cdots (n-k+1)}{(k!)^2} c_0, \quad (k = 1, 2, \cdots, n)$$

当  $k = n$  时，最高项系数为：

$$c_n = (-1)^n \frac{1}{n!} c_0,$$

级数解转化为多项式解（拉盖多项式），取

$$c_0 = n!, c_n = (-1)^k$$

拉盖多项式的系数为：

$$c_k = (-1)^k \frac{(n!)^2}{(k!)^2 (n-k)!}, \quad (k = 1, 2, \cdots, n)$$

拉盖多项式:

$$\begin{aligned}
 L_n(x) &= \sum_{k=0}^n c_k x^k = \sum_{k=0}^n (-1)^k \frac{(n!)^2}{(k!)^2 (n-k)!} x^k \\
 &= \sum_{k=0}^n (-1)^k \frac{(n!)}{(k!)(n-k)!} \frac{n!}{k!} x^k \\
 &= \sum_{k=0}^n (-1)^k C_n^k \frac{n!}{k!} x^k, \quad (k = 1, 2, \dots, n)
 \end{aligned}$$

# 拉盖多项式的性质

**性质 1:** 拉盖多项式微分形式

$$L_n(x) = e^x \frac{d^n}{dx^n} (x^n e^{-x})$$

**证明:** 由高阶导数莱布尼兹公式

$$(u \cdot v)^{(n)} = \sum_{k=0}^n C_n^k u^{(k)} v^{(n-k)},$$

得:

$$\begin{aligned} (e^{-x} \cdot x^n)^{(n)} &= \sum_{k=0}^n C_n^k [e^{-x}]^{(k)} [(x^n)^{(n-k)}] \\ &= \sum_{k=0}^n C_n^k [(-1)^k e^{-x}] \left[ C_n^k \frac{n!}{k!} x^k \right] \end{aligned}$$

$$\begin{aligned}
 e^x \frac{d^n}{dx^n} (e^{-x} \cdot x^n) &= e^x \sum_{k=0}^n C_n^k [(-1)^k e^{-x}] [C_n^k \frac{n!}{k!} x^k] \\
 &= \sum_{k=0}^n (-1)^k C_n^k \frac{n!}{k!} x^k \\
 &= L_n(x)
 \end{aligned}$$

证毕!

## 性质 2: 拉盖尔多项式生成函数

$$w(t, x) = \frac{e^{-xt/(1-t)}}{1-t}$$

证明: 对函数在  $t = 0$  做泰勒展开

$$\begin{aligned} w(t, x) &= \sum_{n=0}^{\infty} \frac{d^n w}{dt^n} \Big|_{t=0} \frac{t^n}{n!} \\ &= \sum_{n=0}^{\infty} e^x \frac{d^n}{dx^n} (e^{-x} \cdot x^n) \frac{t^n}{n!} \\ &= \sum_{n=0}^{\infty} L_n \frac{t^n}{n!} \end{aligned}$$

### 性质 3: 拉盖尔多项式递推式

$$L_{n+1} = (2n + 1 - x)L_n - n^2 L_{n-1}$$

$$L_1 = (1 - x)L_0$$

**证明:** 对  $w$  函数就  $t$  求偏导,

$$\frac{\partial w}{\partial t} = \left[ \frac{1}{(1-t)^2} - \frac{x}{(1-t)^3} \right] e^{-xt/(1-t)}$$

$$(1-t)^2 \frac{\partial w}{\partial t} = [1-t-x]w, \dots \dots (1)$$

对  $w$  函数的展开式就  $t$  求偏导,

$$\begin{aligned}\frac{\partial w}{\partial t} &= \sum_{n=1}^{\infty} L_n \frac{t^{n-1}}{(n-1)!} \\ &= \sum_{n=0}^{\infty} L_{(n+1)} \frac{t^n}{(n)!} \\ &= \sum_{n=2}^{\infty} L_{(n-1)} \frac{t^{n-2}}{(n-2)!}\end{aligned}$$

代入 (1) 式的左边, 有:

$$(1-t)^2 \frac{\partial w}{\partial t} = \sum_{n=0}^{\infty} L_{n+1} \frac{t^n}{(n)!} - 2 \sum_{n=1}^{\infty} L_n \frac{t^n}{(n-1)!} + \sum_{n=2}^{\infty} L_{n-1} \frac{n(n-1)}{(n)!} t^n$$



(1) 式的右边, 有:

$$\begin{aligned}
 [1 - t - x]w &= (1 - x)w - tw \\
 &= \sum_{n=0}^{\infty} (1 - x)L_n \frac{t^n}{n!} - \sum_{n=0}^{\infty} L_n \frac{t^{n+1}}{n!} \\
 &= \sum_{n=0}^{\infty} (1 - x)L_n \frac{t^n}{n!} - \sum_{n=1}^{\infty} L_{n-1} \frac{t^n}{(n-1)!}
 \end{aligned}$$

(1) 式的左边 = 右边, 整理得递推式!

**性质 4:** 拉盖多项式归一性

**证明:** 有递推式

$$L_{n+1} = (2n + 1 - x)L_n - n^2 L_{n-1}$$

$$L_n = (2n - 1 - x)L_{n-1} - (n - 1)^2 L_{n-2}$$

$$L_n^2 = (2n - 1 - x)L_n L_{n-1} - (n - 1)^2 L_n L_{n-2}$$

$$L_{n-1} L_{n+1} = (2n + 1 - x)L_{n-1} L_n - n^2 L_{n-1}^2$$

$$\int_0^\infty e^{-x} L_n^2 dx = n^2 \int_0^\infty e^{-x} L_{n-1}^2 dx$$

$$= (n!)^2 \int_0^\infty e^{-x} L_0^2 dx$$

$$= (n!)^2$$

**性质 5:** 拉盖尔多项式正交性

**证明:** 拉盖尔多项式满足拉盖方程:

$$xL_n'' + [1 - x]L_n' + nL_n = 0$$

$$[xe^{-x}L_n']' + ne^{-x}L_n = 0$$

$$[xe^{-x}L_m']' + me^{-x}L_m = 0$$

$$L_m[xe^{-x}L_n']' + ne^{-x}L_mL_n = 0$$

$$L_n[xe^{-x}L_m']' + me^{-x}L_nL_m = 0$$

$$\begin{aligned} (m - n) \int_0^\infty e^{-x} L_n L_m dx &= \int_0^\infty [L_n [xe^{-x} L_m']' - L_m [xe^{-x} L_n']'] dx \\ &= - \int_0^\infty [L_n' [xe^{-x} L_m'] + L_m' [xe^{-x} L_n']] dx \\ &= \int_0^\infty [xe^{-x} L_m' L_n' - xe^{-x} L_n' L_m'] dx = 0 \end{aligned}$$

# 广义拉盖方程多项式

量子力学定义广义拉盖多项式为：

$$L_n^0(x) = \frac{1}{n!} L_n(x) = \frac{1}{n!} \sum_{k=0}^n (-1)^k C_n^k \frac{n!}{k!} x^k$$

$$L_n^m(x) = \frac{1}{n!} \sum_{k=0}^n (-1)^k C_n^k \frac{(n+m)!}{(m+k)!} x^k$$

微分形式：

$$L_n^m(x) = \frac{x^{-m} e^x}{n!} \frac{d^n}{dx^n} (x^{m+n} e^{-x})$$

递推式:

$$(n+1)L_{n+1}^m = (2n+1+m-x)L_n^m - (n+m)L_{n-1}^m$$

正交性:

$$\int_0^\infty e^{-x} x^m L_n^m L_k^m dx = 0, \quad (k \neq n)$$

归一性:

$$\int_0^\infty e^{-x} x^m [L_n^m]^2 dx = \frac{(n+m)!}{n!}$$

归一性推论:

$$\int_0^\infty e^{-x} x^{m+1} [L_n^m]^2 dx = \frac{(n+m)!}{n!} (2n+m+1)$$

氢原子径向解:

$$R_{nl}(r) = N_{nl}R(r) = N_{nl}\xi^l L_{n-l-1}^{2l+1}(\xi)e^{-\xi/2}, \quad (\xi = \alpha r)$$

能量固有值:

$$n = \beta = \frac{2\mu e_s^2}{\alpha \hbar^2}$$

$$E_n = -\frac{1}{n^2} \frac{\mu e_s^4}{2\hbar^2} = \frac{E_1}{n^2}$$

氢原子的解:

$$\Psi(r, \theta, \varphi) = R_{nl}(r)Y_{lm}(\theta, \varphi)$$

求归一化系数  $N_{nl}$ 

$$\iiint \Psi(r, \theta, \varphi) d\tau = 1$$

$$\iiint |N_{nl} R(r) Y_{lm}(\theta, \varphi)|^2 r^2 \sin \theta dr d\theta d\varphi = 1$$

$$\int_0^\infty N_{nl}^2 R^2(r) r^2 dr = 1$$

$$\frac{1}{\alpha^3} \int_0^\infty N_{nl}^2 R^2(\xi) \xi^2 d\xi = 1$$

$$\frac{1}{\alpha^3} \int_0^\infty N_{nl}^2 \xi^{2l+2} [L_{n-l-1}^{2l+1}(\xi)]^2 e^{-\xi} d\xi = 1$$

$$\frac{1}{\alpha^3} \int_0^\infty N_{nl}^2 \xi^{M+1} [L_N^M(\xi)]^2 e^{-\xi} d\xi = 1$$

$$\frac{1}{\alpha^3} N_{nl}^2 \frac{(N+M)!}{N!} (2N+M+1) = 1$$

→

$$N_{nl}^2 \frac{2n(n+1)!}{\alpha^3(n-l-1)!} = 1$$

$$N_{nl} = \sqrt{\alpha^3 \frac{(n-l-1)!}{2n(n+1)!}}$$



# 作业

- 1、证明拉盖尔多项式的正交性
- 2、求方程的解

$$\frac{d^2 U}{d\xi^2} + \frac{2}{\xi} \frac{dU}{d\xi} + \left[ \frac{\beta}{\xi} - \frac{l(l+1)}{\xi^2} \right] U = 0$$

- 3、计算积分:

$$\int_0^\infty e^{-x} (L_1(x))^2 dx, \quad \int_0^\infty e^{-x} (L_2(x))^2 dx,$$