# 角动量算符

# 角动量算符的本征值和本征态

角动量算符（轨道角动量）的定义是：

$$\hat{\vec{L}} = \hat{\vec{r}} \times \hat{\vec{p}} = -\mathrm{i}\hbar \vec{r} \times \vec{\nabla},$$

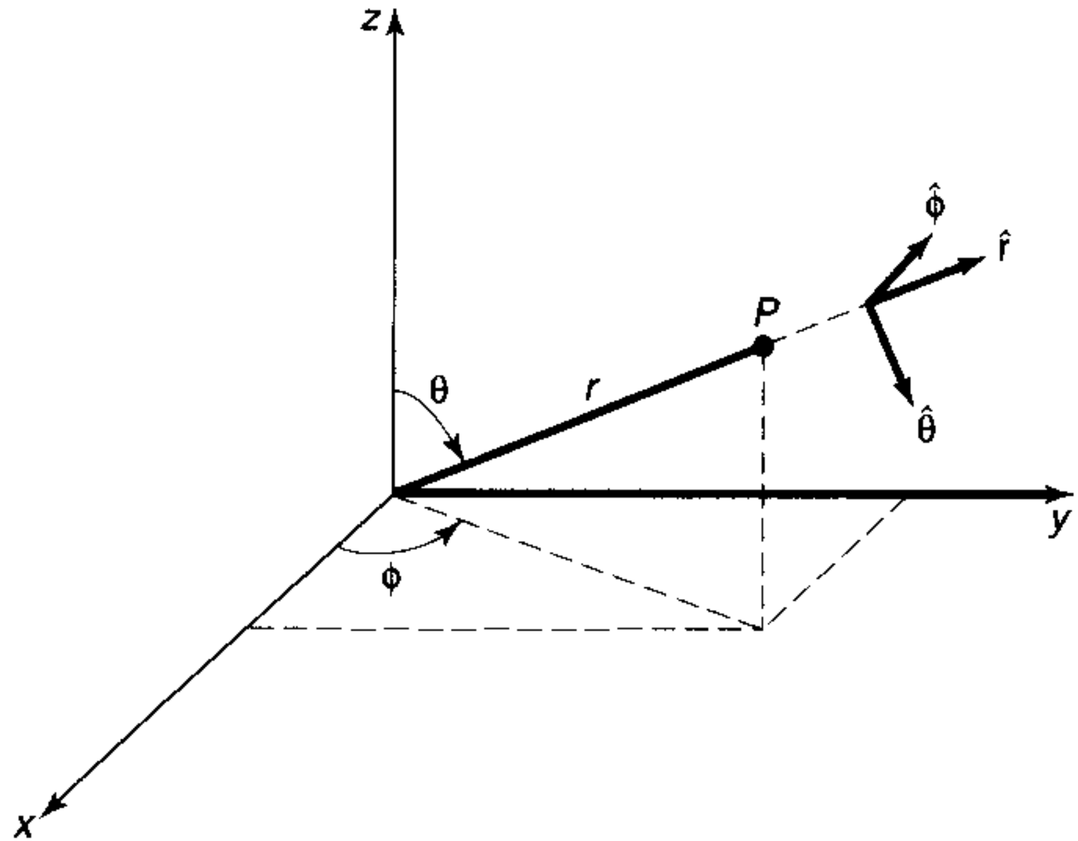
$$\hat{L}_x = -\mathrm{i}\hbar\left( y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y} \right), \cdots.$$

$$\hat{L^2} \equiv \hat{\vec{L}^2} = \hat{L}_x{}^2 + \hat{L}_y{}^2 + \hat{L}_z{}^2.$$

更方便的是变换到球坐标　$(r, \theta, \varphi)$

$$x = r\sin\theta\cos\varphi, \quad y = r\sin\theta\sin\varphi, \quad z = r\cos\theta,$$

$$r \in [0, \infty), \quad \theta \in [0, \pi], \quad \varphi \in [0, 2\pi),$$




球坐标系

# 回顾：角动量算符的球坐标表示

$$
\begin{cases}
\hat{\vec{\mathrm{L}}} = -\mathrm{i}\hbar\left(\vec{\mathrm{e}}_{\varphi}\dfrac{\partial}{\partial\theta} - \vec{\mathrm{e}}_{\theta}\dfrac{1}{\sin\theta}\dfrac{\partial}{\partial\varphi}\right) \\
\hat{L}_x = i\hbar\left(\sin\varphi\dfrac{\partial}{\partial\theta} + \cot\theta\cos\varphi\dfrac{\partial}{\partial\varphi}\right) \\
\hat{L}_y = i\hbar\left(-\cos\varphi\dfrac{\partial}{\partial\theta} + \cot\theta\sin\varphi\dfrac{\partial}{\partial\varphi}\right) \\
\hat{L}_z = -i\hbar\dfrac{\partial}{\partial\varphi}
\end{cases}
$$

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

# $L_z$的本征值和本征函数

记 $\hat{L}_z$ 的本征值为 $m\hbar$, 本征函数为 $\psi_m(\varphi)$, 则本征方程是：

$$\hat{L}_z\psi_m = m\hbar\psi_m,$$

$$\frac{d\psi_m}{d\varphi} = \mathrm{i}\, m\psi_m(\varphi),$$

$$\psi_m(\varphi) = C\exp(im\varphi).$$

由波函数的连续性，必须有： $\psi_m(\varphi+2\pi) = \psi_m(\varphi),$

所以 $\quad e^{im(\varphi+2\pi)} = e^{im\varphi} \qquad m = 0, \pm 1, \pm 2, \cdots$

周期性边界条件

归一化条件是：

$$\int_0^{2\pi} \left|\psi_m(\varphi)\right|^2 d\varphi = 1, \quad \rightarrow \quad C = \frac{1}{\sqrt{2\pi}}.$$

## $L^2$的本征值和本征函数

$\hat{L}^2$ 的本征函数是 $(\theta,\varphi)$ 的函数, 记为 $Y(\theta,\varphi)$ , 本征值记为 $\lambda\hbar^2$,

$$\hat{L}^2 Y = \lambda\hbar^2 Y,$$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2} = -\lambda Y(\theta,\varphi).$$

求上述方程的分离变量的解，也就是设

$$\mathrm{Y}(\theta,\phi) = \mathrm{P}(\theta)\Phi(\phi)$$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2}=-\lambda Y(\theta,\varphi).$$

分离变量求解，

$$\mathrm{Y}(\theta,\phi)=\mathrm{P}(\theta)\Phi(\phi)$$

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

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

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

$$\frac{1}{\mathrm{P}}\sin\theta\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{dP}}{\mathrm{d}\theta}\right)+\lambda\sin^2\theta=\mathrm{m}^2$$

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{dP}{d\theta}\right)-\frac{m^2}{\sin^2\theta}P(\theta)=-\lambda P(\theta).$$

引入 $w=\cos\theta,\qquad w\in[-1,+1]$ $\boxed{\text{为何不用}\sin\theta?}$

$$\frac{d}{dw}\left[(1-w^2)\frac{dP}{dw}\right]+\left(\lambda-\frac{m^2}{1-w^2}\right)P(w)=0.$$

称为缔合Legendre方程。$w=\pm1$是这个方程的“奇点”，除非$\lambda$取某些特定值，方程的解将在 $w=\pm1$处变成无穷大

$\lambda$的这些允许值是： $\lambda=l(l+1).\qquad l=|m|,|m|+1,\cdots$

把对应的解记为 $P_l^m(w)$， $|m|\le l$

在$0\le\theta<\pi$内是有界的，是物理上允许的解

（参见曾谨言书附录）

$$\frac{d}{dw}\left[(1-w^2)\frac{dP_l^m}{dw}\right]+\left(l(l+1)-\frac{m^2}{1-w^2}\right)P_l^m(w)=0.$$

当$m=0$时，$P_l(w)\equiv P_l^{m=0}(w)$满足

$$\frac{d}{dw}\left[(1-w^2)\frac{dP_l}{dw}\right]+l(l+1)P_l(w)=0.$$

这个方程称为Legendre方程，它的解$P_l(w)$是$w$的$l$阶多项式，称为Legendre多项式，定义为：

$$P_l(w)=\frac{1}{2^l\,l!}\frac{d^l}{dw^l}(w^2-1)^l.$$

$P_l^m(w)$ 称为缔合Legendre函数，定义是：

$$P_l^m(w)=\frac{1}{2^l\,l!}(1-w^2)^{m/2}\frac{d^{l+m}}{dw^{l+m}}(w^2-1)^l.$$

Legendre多项式，根据$l$的奇偶决定是奇函数还是偶函数：

$$P_0(x)=1,\ P_1(x)=\frac{1}{2}\frac{d}{dx}(x^2-1)=x,$$

$$P_2(x)=\frac{1}{4\cdot 2}\left(\frac{d}{dx}\right)^2(x^2-1)^2=\frac{1}{2}(3x^2-1),$$

于是，

$$P_2^0(x)=\frac{1}{2}(3x^2-1),$$

$$P_2^1(x)=(1-x^2)^{1/2}\frac{d}{dx}\left[\frac{1}{2}(3x^2-1)\right]=3x\sqrt{1-x^2},$$

$$P_2^2(x)=(1-x^2)\left(\frac{d}{dx}\right)^2\left[\frac{1}{2}(3x^2-1)\right]=3(1-x^2),$$

$$P_1^1 = \sin\theta$$

$$P_1^0 = \cos\theta$$

$$P_2^2 = 3\sin^2\theta$$

$$P_2^1 = 3\sin\theta\cos\theta$$

$$P_2^0 = \tfrac{1}{2}(3\cos^2\theta - 1)$$

$$P_3^3 = 15\sin\theta(1-\cos^2\theta)$$

$$P_3^2 = 15\sin^2\theta\cos\theta$$

$$P_3^1 = \tfrac{3}{2}\sin\theta(5\cos^2\theta - 1)$$

$$P_3^0 = \tfrac{1}{2}(5\cos^3\theta - 3\cos\theta)$$

$P_l^{-m}$怎么表示?

$$\boxed{P_l^{-m}(x) = (-1)^m \frac{(l-m)!}{(l+m)!} P_l^m(x)}$$

轨道角动量的本征函数最后成为：

$$Y_{lm}(\theta,\varphi) = N_{lm} P_l^m(\cos\theta)\exp(\mathrm{i}\, m\varphi),$$

$$l = 0,1,2\cdots; \qquad m = l, l-1, \cdots, -l.$$

$$N_{lm}: \quad \int Y_{lm}^*(\theta,\varphi)\cdot Y_{lm}(\theta,\varphi)\cdot d\Omega = 1. \qquad (d\Omega = \sin\theta\, d\theta\, d\varphi)$$

利用$P_l^m$的正交归一性：

$$\int_0^\pi d\theta \sin\theta P_l^m\left(\cos\theta\right) P_{l'}^m\left(\cos\theta\right)$$

$$= \frac{2}{\left(2l+1\right)} \frac{\left(l+m\right)!}{\left(l-m\right)!} \delta_{l,l'}$$

得： $$N_{lm} = (-1)^m \sqrt{\frac{(2l+1)}{4\pi} \frac{(l-m)!}{(l+m)!}}.$$

$Y_{lm}(\theta,\varphi)$ 称为球谐函数，$l$ 称为角量子数，$m$ 称为磁量子数

采用原子物理的术语：

$l = 0,1,2,3,\cdots$ 的状态分别称为S, P, D, F, …态。

对于指定的 $l$,有$2l+1$个不同的m值, 这就是 $\hat{L}^2$ 的本征值 $l(l+1)\hbar^2$ 的简并度

$$Y_0^0 = \left(\frac{1}{4\pi}\right)^{1/2} \qquad Y_2^{\pm 2} = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta e^{\pm 2i\phi}$$

$$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta \qquad Y_3^0 = \left(\frac{7}{16\pi}\right)^{1/2} (5\cos^3\theta - 3\cos\theta)$$

$$Y_1^{\pm 1} = \mp\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{\pm i\phi} \qquad Y_3^{\pm 1} = \mp\left(\frac{21}{64\pi}\right)^{1/2} \sin\theta(5\cos^2\theta - 1)e^{\pm i\phi}$$

$$Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1) \qquad Y_3^{\pm 2} = \left(\frac{105}{32\pi}\right)^{1/2} \sin^2\theta\cos\theta e^{\pm 2i\phi}$$

$$Y_2^{\pm 1} = \mp\left(\frac{15}{8\pi}\right)^{1/2} \sin\theta\cos\theta e^{\pm i\phi} \qquad Y_3^{\pm 3} = \mp\left(\frac{35}{64\pi}\right)^{1/2} \sin^3\theta e^{\pm 3i\phi}$$

## 球谐函数的基本性质

(1) $Y_{lm}(\theta,\varphi)$ 是 $\hat{L}^2$ 和 $\hat{L}_z$ 的共同本征函数：

$$\boxed{\begin{cases} \hat{L}^2 Y_{lm} = l(l+1)\hbar^2 Y_{lm}, & (l = 0,1,2,\cdots) \\ \hat{L}_z Y_{lm} = m\hbar Y_{lm}. & (m = l, l-1, \cdots, -l) \end{cases}}$$

(2) 正交归一性

$$\int Y^*_{l'm'}(\theta,\varphi)\cdot Y_{lm}(\theta,\varphi)\cdot d\Omega = \delta_{l'l}\delta_{m'm}.$$

（3）关于宇称的定义也可以推广到三维空间。变换

$$\vec{r} \to -\vec{r} \quad (x \to -x, y \to -y, z \to -z)$$

称为“空间反射”变换。如果波函数满足

$$\psi(-\vec{r}) = \pm\psi(\vec{r})$$ 称反射对称或反对称

在球坐标系中，空间反射变换成为

$$r \to r,\ \theta \to \pi - \theta,\ \varphi \to \pi + \varphi$$

球谐函数在空间反射下的变换是

$$Y_{lm}(\pi - \theta, \pi + \varphi) = (-1)^l Y_{lm}(\theta, \varphi)$$

$Y_{lm}(\theta, \varphi)$ 的宇称是 $(-1)^l$

（4）球谐函数$Y_{lm}(\theta,\varphi)$是单位球面（$r=1$）上的完备函数系，以$(\theta,\varphi)$为变量的任何函数都可以展开为$Y_{lm}(\theta,\varphi)$的线性组合。

（5）一些递推关系：

$$\cos\theta Y_{lm}=\sqrt{\frac{(l+1)^2-m^2}{(2l+1)(2l+3)}}Y_{l+1,m}+\sqrt{\frac{l^2-m^2}{(2l-1)(2l+1)}}Y_{l-1,m}$$

$$\sin\theta e^{\pm i\varphi}Y_{lm}=\mp\sqrt{\frac{(l\pm m+1)(l\pm m+2)}{(2l+1)(2l+3)}}Y_{l+1,m\pm1}\pm\sqrt{\frac{(l\mp m)(l\mp m-1)}{(2l-1)(2l+1)}}Y_{l-1,m\pm1}$$