

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：

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

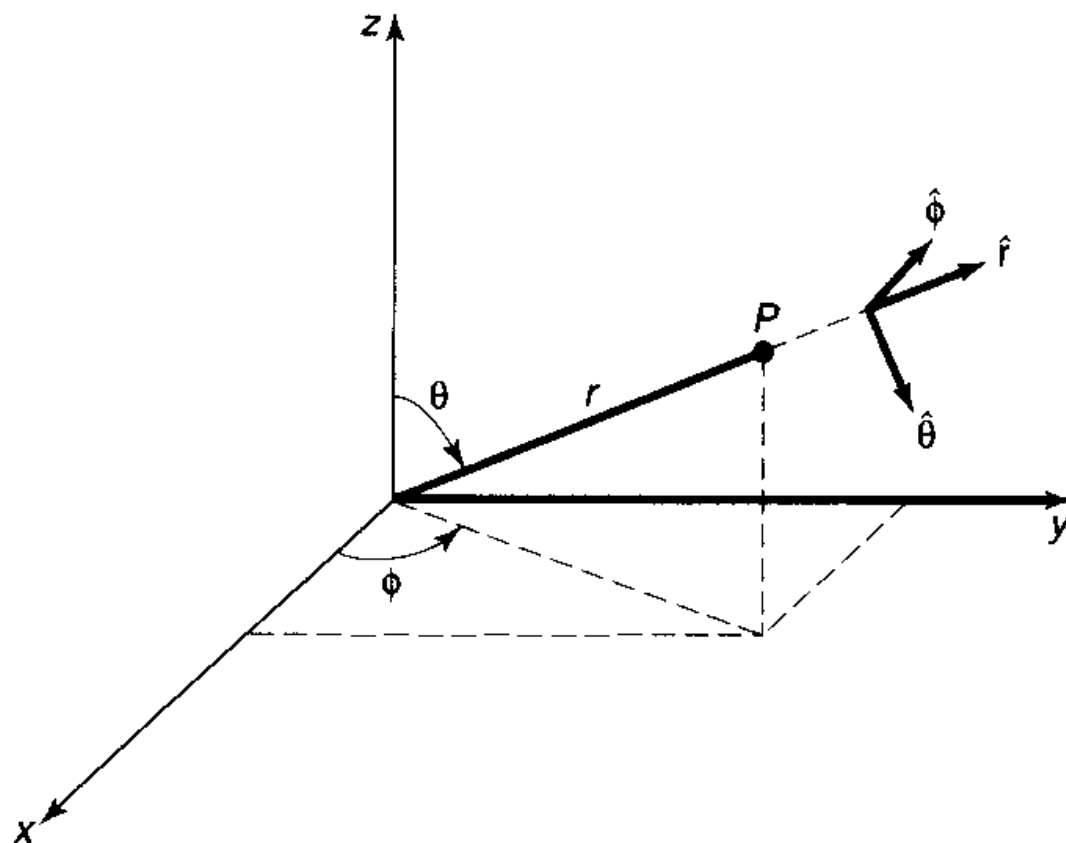
$$\hat{L}_x = -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right), \dots$$

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

更方便的是变换到球坐标 (r, θ, φ)

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

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



球坐标系

回顾：角动量算符的球坐标表示

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

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

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:

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

$$\frac{d\psi_m}{d\varphi} = im \psi_m(\varphi),$$

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

由波函数的单值性, 必须有: $\psi_m(\varphi + 2\pi) = \psi_m(\varphi)$,

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

周期性边界条件

归一化条件是：

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

L^2 的本征值和本征函数

\hat{L}^2 的本征函数是 (θ, φ) 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

$$Y(\theta, \phi) = P(\theta)\Phi(\phi)$$

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

分离变量求解,

$$Y(\theta, \phi) = P(\theta)\Phi(\phi)$$

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

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

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

引入 $w = \cos \theta, \quad w \in [-1, +1]$

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

称为**缔合Legendre方程**。 $w = \pm 1$ 是这个方程的“奇点”，除非 λ 取某些特定值，方程的解将在 $w = \pm 1$ 处变成无穷大

λ 的这些允许值是： $\lambda = l(l+1), \quad l = |m|, |m|+1, \dots$

把对应的解记为 $P_l^m(w) \quad |m| \leq l$

在 $0 \leq \theta < \pi$ 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：

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

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

于是，

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

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

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

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

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

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

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

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

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

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

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

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

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

轨道角动量的本征函数最后成为：

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

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

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

利用 P_l^m 的正交归一性：

$$\begin{aligned} & \int_0^\pi d\theta \sin \theta P_l^m(\cos \theta) P_{l'}^m(\cos \theta) \\ &= \frac{2}{(2l+1)} \frac{(l+m)!}{(l-m)!} \delta_{l,l'} \end{aligned}$$

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

$Y_{lm}(\theta, \varphi)$ 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:

$l = 0, 1, 2, 3, \dots$ 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

$$Y_{00} = \sqrt{\frac{1}{4\pi}}, \quad Y_{10} = \sqrt{\frac{3}{4\pi}} \cos \theta,$$

$$Y_{1,\pm 1} = \mp \sqrt{\frac{3}{8\pi}} \sin \theta \exp(\pm i \varphi).$$

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:

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

(2) 正交归一性

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

$$Y_0^0 = \left(\frac{1}{4\pi}\right)^{1/2}$$

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

$$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} \cos \theta$$

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

$$Y_1^{\pm 1} = \mp \left(\frac{3}{8\pi}\right)^{1/2} \sin \theta e^{\pm i\phi}$$

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

$$Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2} (3 \cos^2 \theta - 1)$$

$$Y_3^{\pm 2} = \left(\frac{105}{32\pi}\right)^{1/2} \sin^2 \theta \cos \theta e^{\pm 2i\phi}$$

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

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

(3) 关于宇称的定义也可以推广到三维空间。变换

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

称为“**空间反射**”变换。如果波函数满足

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

在球坐标系中，空间反射变换成为

$$r \rightarrow r, \quad \theta \rightarrow \pi - \theta, \quad \varphi \rightarrow \pi + \varphi$$

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 (θ, φ) 为变量的任何函数都可以展开为 $Y_{lm}(\theta, \varphi)$ 的线性组合。