# 量子力学与统计物理

# Quantum mechanics and statistical physics

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# 第三章：量子力学中的力学量

## 第三讲：常见力学量算符的本征值问题

# 平均值的计算：

设$\psi(x)$为归一化的波函数，求平均值的方法有：

方法1：

直接积分法

$$\bar{A}=\langle\hat{A}\rangle=\int\psi^*(x)\hat{A}\psi(x)\mathrm{d}x$$

方法2：

本征值求和法

$$\bar{A}=\langle\hat{A}\rangle=\sum_n|c_n|^2a_n$$

$$\hat{A}\phi_n=a_n\phi_n,\ \psi(x)=\sum_n c_n\phi_n$$

两种方法的等致性：

$$\overline{A} = \langle \hat{A} \rangle = \int \psi^*(x) \hat{A} \psi(x) \mathrm{d}x$$

$$= \int [\sum_n c_n \phi_n(x)]^* \hat{A} [\sum_m c_m \phi_m(x)] \mathrm{d}x$$

$$= \sum_{m,n} c_n^* c_m \int \phi_n^*(x) \hat{A} \phi_m(x) \mathrm{d}x$$

$$= \sum_{m,n} c_n^* c_m a_m \int \phi_n^*(x) \phi_m(x) \mathrm{d}x$$

$$= \sum_{m,n} c_n^* c_m a_m \delta_{nm} = \sum_n |c_n|^2 a_n$$

若波函数还没有归一化，则平均值为

$$\overline{A} = \langle \hat{A} \rangle = \frac{\int \psi^*(x)\hat{A}\psi(x)\mathrm{d}x}{\int \psi^*(x)\psi(x)\mathrm{d}x} = \frac{\sum_n |c_n|^2 a_n}{\sum_n |c_n|^2}$$

# 若本征值含连续谱

$$\psi(x)=\sum_n c_n\phi_n(x)+\int c_\lambda\phi_\lambda(x)\mathrm{d}\lambda$$

$$c_n=\int\phi_n^*(x)\psi(x)\mathrm{d}x,\ c_\lambda=\int\phi_\lambda^*(x)\psi(x)\mathrm{d}x$$

正交归一化：$\sum_n|c_n|^2+\int|c_\lambda|^2\,\mathrm{d}\lambda=1$

$$\overline{A}=\langle\hat{A}\rangle=\sum_n|c_\mathrm{n}|^2a_n+\int|c_\lambda|^2a_\lambda\mathrm{d}\lambda$$

$$\overline{A}=\langle\hat{A}\rangle=\int\psi^*(x)\hat{A}\psi(x)\mathrm{d}x$$

$|c_n|^2\to$ 概率；$|c_\lambda|^2\to$ 概率密度

**总 之：**

不管体系处于本征态还是非本征态， 求解力学量算符的本征值问题，是了解体系的最有效方法。

因此，要掌握常用力学量算符（如坐标、动量、角动量等）本征值问题的求解方法，求出其本征值和本征函数

## （一）动量算符

$$\hat{\boldsymbol{p}} = -\mathrm{i}\hbar\nabla$$

本征方程 $\hat{\boldsymbol{p}}\psi_{\boldsymbol{p}} = \boldsymbol{p}\psi_{\boldsymbol{p}}$

$$\hat{p}_x\psi_{p_x} = p_x\psi_{p_x}$$

$$-\mathrm{i}\hbar\frac{\partial}{\partial x}\psi_{p_x} = p_x\psi_{p_x}$$

$$\frac{1}{\psi_{p_x}}\frac{\partial}{\partial x}\psi_{p_x} = \frac{\mathrm{i}p_x}{\hbar}$$

$$\psi_{p_x} = \frac{1}{\sqrt{2\pi\hbar}}\exp(\mathrm{i}p_x x/\hbar)$$

本征值为 $\boldsymbol{p}$ 的**本征函数**

$$\psi_{\boldsymbol{p}}(\boldsymbol{r}) = \frac{1}{(2\pi\hbar)^{3/2}}\exp(\frac{\mathrm{i}}{\hbar}\boldsymbol{p}\cdot\boldsymbol{r})$$

平面波归一化计算，前面讲过

本征值谱连续，区间 $(-\infty,+\infty)$ 内所有实数

正交归一性
$$(\psi_{\boldsymbol{p}'}(\boldsymbol{r}),\ \psi_{\boldsymbol{p}}(\boldsymbol{r})) = \int_{-\infty}^{+\infty}\psi_{\boldsymbol{p}'}^*(\boldsymbol{r})\psi_{\boldsymbol{p}}(\boldsymbol{r})\mathrm{d}^3\boldsymbol{r} = \delta^{(3)}(\boldsymbol{p}'-\boldsymbol{p})$$

完备性
$$\int_{-\infty}^{+\infty}\psi_{\boldsymbol{p}}^*(\boldsymbol{r})\psi_{\boldsymbol{p}}(\boldsymbol{r}')\mathrm{d}^3\boldsymbol{p} = \delta^{(3)}(\boldsymbol{r}-\boldsymbol{r}')$$

## （二）位置算符 在位置波函数空间有：$\hat{x} = x$

$$\hat{x}\phi_\lambda = x\phi_\lambda = \lambda\phi_\lambda$$

本征方程

$$x\phi_\lambda = \lambda\phi_\lambda \Rightarrow \begin{cases} \phi_\lambda \neq 0, & x = \lambda \\ \phi_\lambda = 0, & x \neq \lambda \end{cases}$$

因为$\lambda$是常数，除了$x$=$\lambda$这一点外，$x$取其他任何值都有 $\phi_\lambda = 0$

即：$\phi_\lambda(x) = A\delta(x-\lambda)$ 归一化常数：$A = 1$

属于本征值$\lambda$的**本征函数**：

$$\boxed{\phi_\lambda(x) = \delta(x-\lambda)}$$

$$f(x)\delta(x-\lambda) = f(\lambda)\delta(x-\lambda)$$

本征值谱为连续谱，区间 $(-\infty, +\infty)$ 内所有实数

正交归一性 $(\phi_{\lambda'}, \phi_\lambda) = \int_{-\infty}^{+\infty} \phi_{\lambda'}^*(x)\phi_\lambda(x)\mathrm{d}x = \delta(\lambda'-\lambda)$

完备性 $\int_{-\infty}^{+\infty} \phi_\lambda^*(x')\phi_\lambda(x)\mathrm{d}\lambda = \delta(x'-x)$

课堂作业：试求算符$\hat{F}=-\mathrm{i}\exp(-\mathrm{i}x)\dfrac{\mathrm{d}}{\mathrm{d}x}$的本征函数

解：$\hat{F}$ 的本征方程为

$$\hat{F}\phi=F\phi$$

即 $$-\mathrm{i}\exp(-\mathrm{i}x)\frac{\mathrm{d}}{\mathrm{d}x}\phi=F\phi$$

$$\Rightarrow \frac{\mathrm{d}\phi}{\phi}=\mathrm{i}F\exp(-\mathrm{i}x)\mathrm{d}x=\mathrm{d}[-F\exp(-\mathrm{i}x)]$$

$$\Rightarrow \ln\phi=-F\exp(-\mathrm{i}x)+\ln c$$

$$\Rightarrow \phi=c\exp[-F\exp(-\mathrm{i}x)]$$

## （三）角动量算符

### 1. 角动量算符的具体形式：

$$\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p} \Rightarrow \hat{\boldsymbol{L}} = \hat{\boldsymbol{r}} \times \hat{\boldsymbol{p}} = -\mathrm{i}\hbar \boldsymbol{r} \times \nabla$$

**(I) 直角坐标系**

$$(1)\quad \begin{cases} \hat{L}_x = y\hat{p}_z - z\hat{p}_y = -\mathrm{i}\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \\ \hat{L}_y = z\hat{p}_x - x\hat{p}_z = -\mathrm{i}\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \\ \hat{L}_z = x\hat{p}_y - y\hat{p}_x = -\mathrm{i}\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \end{cases}$$

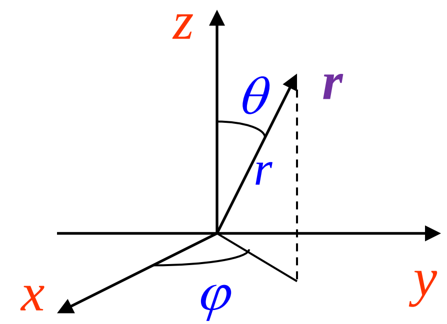
$$\hat{\boldsymbol{L}}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

$$= (y\hat{p}_z - z\hat{p}_y)^2 + (z\hat{p}_x - x\hat{p}_z)^2 + (x\hat{p}_y - y\hat{p}_x)^2 \qquad (2)$$

$$= -\hbar^2\left[\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)^2 + \left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)^2 + \left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)^2\right]$$

## (2) 球坐标系

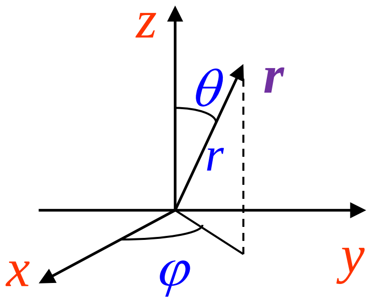
$$\begin{cases} x = r\sin\theta\cos\varphi \\ y = r\sin\theta\sin\varphi, \\ z = r\cos\theta \end{cases} \quad \begin{cases} r = (x^2+y^2+z^2)^{1/2}, & \text{(A)} \\ \theta = \arccos(z/r), & \text{(B)} \\ \varphi = \arctan(y/x), & \text{(C)} \end{cases}$$



球 坐 标

$$(3)\quad \begin{cases} \hat{L}_x = i\hbar[\sin\varphi\dfrac{\partial}{\partial\theta} + \cot\theta\cos\varphi\dfrac{\partial}{\partial\varphi}] \\ \hat{L}_y = -i\hbar[\cos\varphi\dfrac{\partial}{\partial\theta} + \cot\theta\sin\varphi\dfrac{\partial}{\partial\varphi}] \\ \hat{L}_z = -i\hbar\dfrac{\partial}{\partial\varphi} \end{cases}$$

$$\hat{L}^2 = -\hbar^2[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta}) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}] \quad (4)$$




# 直角坐标与球坐标之间的变换关系

$$\begin{cases} x = r\sin\theta\cos\varphi \\ y = r\sin\theta\sin\varphi, \\ z = r\cos\theta \end{cases} \quad \begin{cases} r = (x^2+y^2+z^2)^{1/2}, & \text{(A)} \\ \theta = \arccos(z/r), & \text{(B)} \\ \varphi = \arctan(y/x), & \text{(C)} \end{cases}$$

$$(\arccos x)' = -\frac{1}{\sqrt{1-x^2}}$$

$$(\arctan x)' = \frac{1}{1+x^2}$$

对于任意函数 $f(r, \theta, \varphi)$ 求偏导（直角坐标系中），有：

$$\frac{\partial f}{\partial x_i} = \frac{\partial r}{\partial x_i}\frac{\partial f}{\partial r} + \frac{\partial \theta}{\partial x_i}\frac{\partial f}{\partial \theta} + \frac{\partial \varphi}{\partial x_i}\frac{\partial f}{\partial \varphi}$$

式中： $x_1, x_2, x_3 = x, y, z$

$$\begin{cases} \frac{\partial}{\partial x} = \frac{\partial r}{\partial x}\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial x}\frac{\partial}{\partial \theta} + \frac{\partial \varphi}{\partial x}\frac{\partial}{\partial \varphi} \\ \frac{\partial}{\partial y} = \frac{\partial r}{\partial y}\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial y}\frac{\partial}{\partial \theta} + \frac{\partial \varphi}{\partial y}\frac{\partial}{\partial \varphi} \\ \frac{\partial}{\partial z} = \frac{\partial r}{\partial z}\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial z}\frac{\partial}{\partial \theta} + \frac{\partial \varphi}{\partial z}\frac{\partial}{\partial \varphi} \end{cases} \quad \text{(D)}$$

对(A)式偏导

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

对(B)式偏导

$$\begin{cases} \frac{\partial \theta}{\partial x} = \frac{1}{r}\cos\theta\cos\varphi \\ \frac{\partial \theta}{\partial y} = \frac{1}{r}\cos\theta\sin\varphi \\ \frac{\partial \theta}{\partial z} = -\frac{1}{r}\sin\theta \end{cases}$$

对(C)式偏导

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

将它们代回(D)式：

$$\begin{cases} \dfrac{\partial}{\partial x} = \sin\theta\cos\varphi\dfrac{\partial}{\partial r} + \dfrac{1}{r}\cos\theta\cos\varphi\dfrac{\partial}{\partial\theta} - \dfrac{1}{r}\dfrac{\sin\varphi}{\sin\theta}\dfrac{\partial}{\partial\varphi} \\ \dfrac{\partial}{\partial y} = \sin\theta\sin\varphi\dfrac{\partial}{\partial r} + \dfrac{1}{r}\cos\theta\sin\varphi\dfrac{\partial}{\partial\theta} + \dfrac{1}{r}\dfrac{\cos\varphi}{\sin\theta}\dfrac{\partial}{\partial\varphi} \\ \dfrac{\partial}{\partial z} = \cos\theta\dfrac{\partial}{\partial r} - \dfrac{1}{r}\sin\theta\dfrac{\partial}{\partial\theta} \end{cases}$$

再把上式代回(1)和(2)式，得：

$$\begin{cases} \hat{L}_x = i\hbar[\sin\varphi\dfrac{\partial}{\partial\theta} + \cot\theta\cos\varphi\dfrac{\partial}{\partial\varphi}] \\ \hat{L}_y = -i\hbar[\cos\varphi\dfrac{\partial}{\partial\theta} + \cot\theta\sin\varphi\dfrac{\partial}{\partial\varphi}] \\ \hat{L}_z = -i\hbar\dfrac{\partial}{\partial\varphi} \end{cases}$$

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

可以看出，球坐标系中，角动量算符只与$\theta$和$\varphi$有关，与 $r$ 无关

原因：平动与转动是可以分离的

## 2. $L_z$算符本征问题

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

因为它只与$\varphi$有关，所以其本征函数应具有如下形式

$$\Phi(\varphi)$$

设它的本征值为$l_z$，则其本征方程可以写成：

$$\hat{L}_z \Phi(\varphi) = l_z \Phi(\varphi)$$

$$\frac{\partial}{\partial \varphi}\Phi(\varphi) = \mathrm{i}\frac{1}{\hbar} l_z \Phi(\varphi) \Rightarrow \Phi(\varphi) = A\exp(\mathrm{i} l_z \varphi / \hbar)$$

由周期性边界条件可得（单值性）：

$$\Phi(\varphi)=\Phi(\varphi+2\pi)$$

$$\Rightarrow \Phi(\varphi)=A\exp(\mathrm{i}l_z\varphi/\hbar)$$

$$=A\exp[\mathrm{i}l_z(\varphi+2\pi)/\hbar]$$

$$\Rightarrow \exp(\mathrm{i}2\pi l_z/\hbar)=1$$

$$\Rightarrow l_z/\hbar=m=0,\pm1,\pm2,\ldots$$

$$\Rightarrow l_z=0,\pm\hbar,\pm2\hbar,\ldots$$

$$\Rightarrow l_z=m\hbar,\ m=0,\pm1,\pm2,\cdots$$

$$\Rightarrow \Phi(\varphi)=A\exp(\mathrm{i}m\varphi)$$

求归一化常数：

$$\int_0^{2\pi}\Phi^*\Phi\,\mathrm{d}\varphi=1$$

$$\Rightarrow \int_0^{2\pi}A^2\mathrm{d}\varphi=2\pi A^2=1$$

$$\Rightarrow A=1/\sqrt{2\pi}$$

$$\Rightarrow$$

$$\Phi_m(\varphi)=\frac{1}{\sqrt{2\pi}}\exp(\mathrm{i}m\varphi),$$

$$m=0,\pm1,\pm2,\ldots$$

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

本征方程： $\hat{L}_z \Phi_m(\varphi) = m\hbar \Phi_m(\varphi)$

量子数： $m = 0, \pm 1, \pm 2, \cdots$

本征值： $m\hbar$

本征函数： $\boxed{\Phi_m(\varphi) = \frac{1}{\sqrt{2\pi}} \exp(\mathrm{i}m\varphi)}$

正交归一性： $(\Phi_{m'}(\varphi),\ \Phi_m(\varphi)) = \delta_{m'm}$

完备性： $\sum_m \Phi_m^*(\varphi')\Phi_m(\varphi) = \delta(\varphi' - \varphi)$

$$\int_0^{2\pi} \Phi_{m'}^*(\varphi)\Phi_m(\varphi)\mathrm{d}\varphi = \frac{1}{2\pi}\int_0^{2\pi} \exp[\mathrm{i}(m-m')\varphi]\mathrm{d}\varphi = \delta_{m'm}$$

$$\sum_m \Phi_m^*(\varphi')\Phi_m(\varphi) = \frac{1}{2\pi}\sum_m \exp[\mathrm{i}m(\varphi-\varphi')] = \delta(\varphi-\varphi')$$

## 3. $\hat{L}^2$算符的本征值

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

因为它只与 $\theta, \varphi$ 有关，所以其本征函数应具有如下形式

$$Y(\theta, \varphi)$$

设它的本征值为：$L = \lambda\hbar^2$ 则其本征方程可写成：

$$\hat{L}^2 Y(\theta,\varphi) = L\, Y(\theta,\varphi) = \lambda\hbar^2 Y(\theta,\varphi)$$

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

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

此为球面方程（球谐函数方程）。其中 $Y(\theta,\varphi)$ 是 $\hat{L}^2$ 属于本征值 $\lambda\hbar^2$ 的本征函数。利用分离变量法及微分方程的幂级数解法，求球面方程在 $0\le\theta\le\pi,\ 0\le\varphi\le 2\pi$ 区域内的有限单值函数解（其求解方法在数学物理方法中已有详细的讲述），可得

结论：

（1）有非奇异解的条件，量子数为：

$$\lambda = l(l+1),\ l = 0,1,2,3,\ldots$$

（2）方程的解是球谐函数：

$$\boxed{Y_{lm}(\theta,\varphi) = (-1)^m \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}} P_l^m(\cos\theta)\Phi_m(\varphi)}$$

式中，$\Phi_m(\varphi) = \exp(\mathrm{i}m\varphi),\ m = 0,\pm1,\pm2\ldots\pm l,$ $P_l^m$是勒让德多项式

$$P_l^m(\cos\theta) = (-1)^{l+m} \frac{1}{2^l l!} \sqrt{\frac{(2l+1)}{4\pi}} \frac{(l+m)!}{(l-m)!} \frac{1}{\sin^m\theta} \left(\frac{\mathrm{d}}{\mathrm{d}\cos\theta}\right)^{l-m} \sin^{2l}\theta$$

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

本征方程：

$$\hat{L}^2 Y_{lm}(\theta,\varphi) = l(l+1)\hbar^2 Y_{lm}(\theta,\varphi) \qquad \begin{cases} l = 0,1,2,3,\ldots \\ m = 0,\pm1,\pm2\ldots\pm l \end{cases}$$

本征值： $l(l+1)\hbar^2$ 本征函数： $Y_{lm}(\theta,\varphi)$

正交归一性： $\int_0^{\pi}\int_0^{2\pi} Y^*_{l'm'}(\theta,\varphi) Y_{lm}(\theta,\varphi) \sin\theta \mathrm{d}\varphi \mathrm{d}\theta = \delta_{ll'}\delta_{mm'}$

完备性：

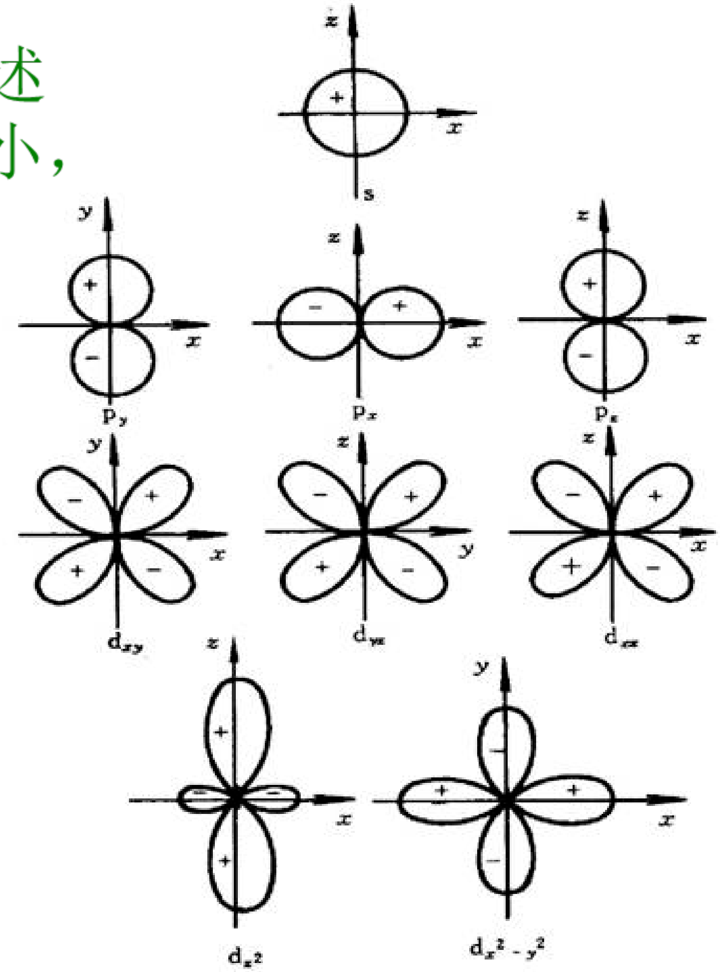
$$\psi(\theta,\varphi) = \sum_{l=0}^{\infty}\sum_{m=-l}^{l} C_{lm} Y_{lm}(\theta,\varphi), \quad C_{lm} = \int_0^{\pi}\int_0^{2\pi} Y^*_{lm}(\theta,\varphi)\psi(\theta,\varphi)\sin\theta \mathrm{d}\varphi \mathrm{d}\theta$$

简并度： $2l+1$

对于同一个本征值 $l(l+1)\hbar^2$，有 $(2l+1)$ 个本征函数 $Y_{lm}$

对于每一个 $l$，一共有 $(2l+1)$ 个 $m = 0,\pm1,\pm2\ldots\pm l$

核外电子能量$E_{nlmm_s}$，$n$描述能级，$l$描述角动量的大小，$m$描述角动量的投影大小，$m_s$描述自旋投影大小，能量简并度$2n^2$



**量子数：**

主量子数： $n = 1, 2, 3, 4, \ldots$

角量子数： $l = 0, 1, 2, \ldots, (n-1)$

磁量子数： $m = 0, \pm 1, \pm 2, \ldots \pm l$

自旋量子数： $m_s = \pm 1/2$

**量子态：**

s 态： $l = 0 \ (m = 0)$

p 态： $l = 1 \ (m = -1, 0, 1 \leftrightarrow \mathrm{p}_x, \mathrm{p}_y, \mathrm{p}_z)$

d 态： $l = 2 \ (m = 0, \pm 1, \pm 2 \leftrightarrow \mathrm{d}_{xy}, \mathrm{d}_{yz}, \mathrm{d}_{zx}, \mathrm{d}_{x^2-y^2}, \mathrm{d}_{z^2})$

f 态： $l = 3 \quad (\ldots)$

## 小结：

$\hat{L}^2$ 的本征值：

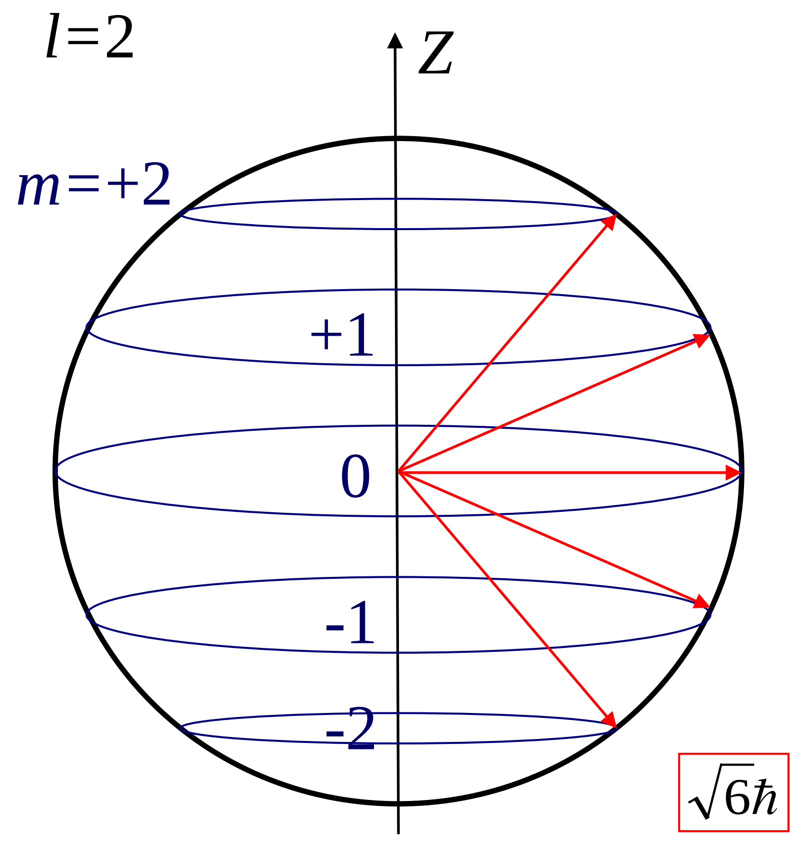
$$\boxed{l(l+1)\hbar^2, l = 1,2,\ldots}$$

确定了角动量的大小

$\hat{L}_z$ 的本征值：

$$\boxed{L_z = m\hbar, m = 0,\pm1,\pm2,\ldots\pm l}$$

确定了角动量的方向
(角动量的投影大小)




角动量的大小量子化

角动量的空间取向也量子化

几个要求记着的球谐函数：

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

$$Y_{00}(\theta,\varphi)=\frac{1}{\sqrt{4\pi}}$$

$$Y_{1\pm1}(\theta,\varphi)=\mp\sqrt{\frac{3}{8\pi}}\sin\theta\exp(\pm\mathrm{i}\varphi)=\mp\sqrt{\frac{3}{8\pi}}\frac{x\pm\mathrm{i}y}{r}$$

$$Y_{10}(\theta,\varphi)=\sqrt{\frac{3}{4\pi}}\cos\theta=\sqrt{\frac{3}{4\pi}}\frac{z}{r}$$

例题：任意态$\psi=\frac{2}{3}Y_{3,1}(\theta,\varphi)+\frac{2}{3}Y_{2,2}(\theta,\varphi)-\frac{1}{3}Y_{1,-1}(\theta,\varphi)$，

求$\psi$态中$L^2, L_z$的可能值、概率及$\overline{L^2}, \overline{L}_z$。

解法：可以看出$\psi$是$\hat{L}^2, \hat{L}_z$的共同本征函数所组成，

列表对应求解：

| | $\hat{L}^2 Y_{lm}(\theta,\varphi)=l(l+1)\hbar^2 Y_{lm}(\theta,\varphi)$ | $\hat{L}_z Y_{lm}(\theta,\varphi)=m\hbar Y_{lm}(\theta,\varphi)$ | $\lvert c\rvert^2$ |
|---|---|---|---|
| $Y_{3,1}$ | $L^2=12\hbar^2$ | $L_z=\hbar$ | $\lvert c_{3,1}\rvert^2=4/9$ |
| $Y_{2,2}$ | $L^2=6\hbar^2$ | $L_z=2\hbar$ | $\lvert c_{2,2}\rvert^2=4/9$ |
| $Y_{1,-1}$ | $L^2=2\hbar^2$ | $L_z=-\hbar$ | $\lvert c_{1,-1}\rvert^2=1/9$ |

$$\overline{L^2}=12\hbar^2\times\frac{4}{9}+6\hbar^2\times\frac{4}{9}+2\hbar^2\times\frac{1}{9}=\frac{74}{9}\hbar^2$$

$$\overline{L}_z=\hbar\times\frac{4}{9}+2\hbar\times\frac{4}{9}+(-\hbar)\times\frac{1}{9}=\frac{11}{9}\hbar$$

例 下列函数哪些是算符$\frac{d^2}{dx^2}$的本征函数，其本征值是什么？

①$x^2$， ② $e^x$， ③$\sin x$， ④$3\cos x$， ⑤$\sin x+\cos x$

解：①$\frac{d^2}{dx^2}(x^2)=2$

∴ $x^2$不是$\frac{d^2}{dx^2}$的本征函数。

② $\frac{d^2}{dx^2}e^x=e^x$

∴ $e^x$是$\frac{d^2}{dx^2}$的本征函数，其对应的本征值为 1。

③ $\frac{d^2}{dx^2}(\sin x)=\frac{d}{dx}(\cos x)=-\sin x$

∴ 可见，$\sin x$ 是 $\frac{d^2}{dx^2}$ 的本征函数，其对应的本征值为－1。

④ $\frac{d^2}{dx^2}(3\cos x)=\frac{d}{dx}(-3\sin x)=-3\cos x$

∴ $3\cos x$ 是 $\frac{d^2}{dx^2}$ 的本征函数，其对应的本征值为－1。

⑤ $\frac{d^2}{dx^2}(\sin x+\cos x)=\frac{d}{dx}(\cos x-\sin x)=-\sin x-\cos x$

$=-(\sin x+\cos x)$

∴ $\sin x+\cos x$ 是 $\frac{d^2}{dx^2}$ 的本征函数，其对应的本征值为－1。

**例题** 平面转子的能量本征值与本征态

**解：** 平面转子的哈密顿为

$$\hat{H}=\frac{\hat{l}_z^2}{2I}=-\frac{\hbar^2}{2I}\frac{\partial^2}{\partial\varphi^2}$$

能量本征方程 $-\dfrac{\hbar^2}{2I}\dfrac{\partial^2}{\partial\varphi^2}\psi=E\psi$

解为

$$\psi_m(\varphi)=\frac{1}{\sqrt{2\pi}}e^{\mathrm{i}m\varphi},m=0,\pm1,\pm2,\cdots$$

能量本征值为 $E_m=\dfrac{m^2\hbar^2}{2I}$

显然，除了$m=0$外，对应一个本征值$E_m$，有两个本征态，能级二重简并。

备注

线速度$\boldsymbol{u}\leftrightarrow$角速度$\boldsymbol{\omega}$

质量$m\leftrightarrow$惯量$I$

动量$\boldsymbol{p}=m\boldsymbol{u}\leftrightarrow$动量矩$\boldsymbol{J}=I\boldsymbol{\omega}$

力$\boldsymbol{f}=\dfrac{\partial\boldsymbol{p}}{\partial t}\leftrightarrow$力矩$M=\dfrac{\partial\boldsymbol{J}}{\partial t}$

动能$T=\dfrac{1}{2}m\boldsymbol{u}^2\leftrightarrow$转动动能$T=\dfrac{1}{2}I\boldsymbol{\omega}^2$

包括特例$\boldsymbol{u}=\boldsymbol{r}\times\boldsymbol{\omega}$, $\boldsymbol{J}=\boldsymbol{r}\times\boldsymbol{p}$

课外思考：如果是空间转子，其能量本征值和本征态又是什么？

**例题** 一维自由粒子的能量本征态

**解：** 一维自由粒子的Hamilton 量为 $H=\frac{\hat{p}_x^2}{2m}=-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}$

本征方程： $-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\psi=E\psi$

本征函数： $\psi\sim e^{\pm ikx}$， $k=\sqrt{2mE}/\hbar\geq 0$

能量本征值： $E=\hbar^2k^2/2m\geq 0$

能级二重简并

作业：1. 求自由粒子的质量流密度

2. 设有算符 $\hat{T}(a)$ ，对任意波函数都有

$$\hat{T}(a)\psi(x)=\psi(x-a)$$

试求它的具体形式

3. 已知转子处于如下态

$$\Psi=\frac{1}{3}Y_{11}(\theta,\phi)+\frac{2}{3}Y_{21}(\theta,\phi)$$

试问：(1) $\Psi$是否是 $L^2$ 的本征态？

(2) $\Psi$是否是 $L_z$ 的本征态？

(3) 求 $L^2$ 的平均值；

(4) 在 $\Psi$ 态中分别测量 $L^2$ 和 $L_z$ 时得到的可能值及其相应的几率。

2. 设有算符 $\hat{T}(a)$ ，对任意波函数都有

$$\hat{T}(a)\psi(x)=\psi(x-a)$$

试求它的具体形式

解： 令 $y=x-a$

$$\psi(y)=\sum_{n}^{+\infty}\frac{1}{n!}\left.\frac{\partial^n\psi(y)}{\partial y^n}\right|_{y=x}(y-x)^n$$

$$=\sum_{n}^{+\infty}\frac{1}{n!}\frac{\partial^n\psi(x)}{\partial x^n}(-a)^n=\sum_{n}^{+\infty}\frac{(-a)^n}{n!}\frac{\partial^n}{\partial x^n}\psi(x)$$

$$=\exp(-a\frac{\partial}{\partial x})\psi(x)\Rightarrow$$

$$\psi(x-a)=\hat{T}(a)\psi(x),$$

$$\hat{T}(a)=\exp(-a\frac{\partial}{\partial x})=\exp(-\frac{\mathrm{i}a\hat{p}_x}{\hbar}),$$

## (iii) 氢原子的波函数

$$\nabla^2\psi = \frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial\psi}{\partial r}) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial\psi}{\partial\theta}) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\varphi^2} = 0$$

$$\nabla = \boldsymbol{e}_r\frac{\partial}{\partial r} + \boldsymbol{e}_\theta\frac{1}{r}\frac{\partial}{\partial\theta} + \boldsymbol{e}_\varphi\frac{1}{r\sin\theta}\frac{\partial}{\partial\varphi}$$

$$\psi_{nlm}(r,\theta,\varphi) = R_{nl}(r)Y_{lm}(\theta,\varphi) = R_{nl}(r)\Theta_{lm}(\theta)\Phi_m(\varphi)$$

$$\int_0^{+\infty}\int_0^{\pi}\int_0^{2\pi}\psi^*_{n'l'm'}\psi_{nlm}r^2\sin\theta\mathrm{d}r\mathrm{d}\theta\mathrm{d}\varphi = \delta_{n'n}\delta_{l'l}\delta_{m'm}$$

$$\psi_{nlm}(r,\theta,\varphi)=R_{nl}(r)Y_{lm}(\theta,\varphi),\ (\psi_{n'l'm'},\ \psi_{nlm})=\delta_{n'n}\delta_{l'l}\delta_{m'm}$$

$$\frac{\partial w}{\partial t}+\nabla\cdot\boldsymbol{j}=0,\quad w=|\psi|^2,\ \boldsymbol{j}=\frac{\mathrm{i}\hbar}{2\mu}(\psi\nabla\psi^*-\psi^*\nabla\psi)$$

$$\nabla=\boldsymbol{e}_r\frac{\partial}{\partial r}+\boldsymbol{e}_\theta\frac{1}{r}\frac{\partial}{\partial\theta}+\boldsymbol{e}_\varphi\frac{1}{r\sin\theta}\frac{\partial}{\partial\varphi}$$

$$\psi_{nlm}(r,\theta,\varphi)=R_{nl}(r)Y_{lm}(\theta,\varphi)=R_{nl}(r)\Theta_{lm}(\theta)\Phi_m(\varphi)$$

$$\boxed{\Phi_m(\varphi)=\frac{1}{\sqrt{2\pi}}\exp(\mathrm{i}m\varphi)}$$

书上p.51，3.3题，提示：波函数$\psi$中，关于变量$r$和$\theta$的函数是实函数，关于$\varphi$的函数由上式给定