《原子物理学》

轨道角动量

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Noether's Theorem

有心力系统（势能具有球对称性）的**角动量**是**守恒**的；角动量守恒律在研究原子时是基本而重要的。如何在量子论的框架中描述角动量？

（猜原子角动量是量子化的，因为波函数角向(θ, ϕ)是局域分布的）

$\boxed{\text{波函数}(r, \theta, \phi)\text{定域} \rightarrow \text{量子数}(n, l, m)}$

复 习

- 算符： $\hat{O}(\vec{r},\vec{p}) = O(\hat{\vec{r}},\hat{\vec{p}}) \xrightarrow[\text{表象}]{\text{位置}} O(\vec{r},-i\hbar\nabla)$

- 平均值： $\bar{O} = <\psi(x)|\hat{O}|\psi(x)> \equiv \iiint \psi^* \hat{O} \psi \, d\vec{r}$

- 测量：对某量子态$|\psi>$测量力学量O，则原$|\psi>$态将有$c_i^* c_i$的几率被塌缩至O的本征态/矢之一$|\varphi_i>$；此时O的测量值为$|\varphi_i>$态所对应的本征值o_i。

$$\begin{cases} |\psi> = \sum_i c_i |\varphi_i>, \quad <\varphi_j|\varphi_i> = \delta_{ij} \\ \hat{O}|\varphi_i(x)> = o_i|\varphi_i(x)> \end{cases}$$

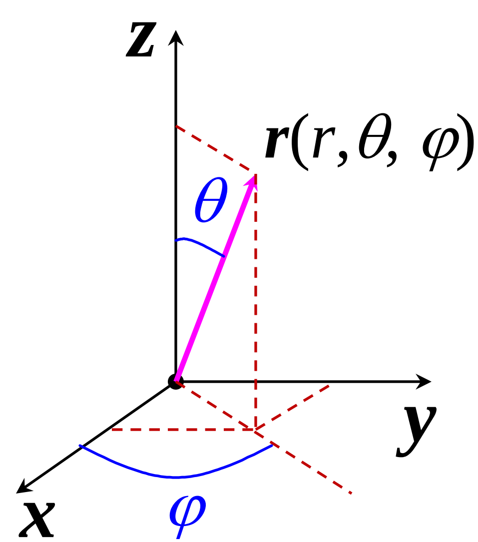
1，轨道角动量算符

轨道角动量及其算符：

$$\boldsymbol{l} = \boldsymbol{r} \times \boldsymbol{p} = \boldsymbol{r} \times \{p_x, p_y, p_z\}$$

$$\hat{\vec{l}} = -i\hbar\vec{r} \times \nabla = -i\hbar \begin{vmatrix} \vec{e}_x & \vec{e}_y & \vec{e}_z \\ x & y & z \\ \partial/\partial x & \partial/\partial y & \partial/\partial z \end{vmatrix} = -i\hbar\{y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}, z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}, x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\}$$

$$= \{y\hat{p}_z - z\hat{p}_y, z\hat{p}_x - x\hat{p}_z, x\hat{p}_y - y\hat{p}_x\}$$



中心力场中，采用球坐标讨论比较方便：

$$\begin{cases} x = r\sin\theta\cos\varphi \\ y = r\sin\theta\sin\varphi \\ x = r\cos\theta \end{cases} \Longleftrightarrow \begin{cases} r = \sqrt{x^2 + y^2 + z^2} \\ \theta = \tan^{-1}(\sqrt{x^2 + y^2}/z) \\ \varphi = \tan^{-1}(y/x) \end{cases}$$

1，轨道角动量算符

- 在球坐标系中表示$\hat{\boldsymbol{l}}$:

分量

$$\begin{cases} \hat{l}_x = i\hbar\left(\sin\varphi\dfrac{\partial}{\partial\theta} + \cot\theta\cos\varphi\dfrac{\partial}{\partial\varphi}\right) \\ \hat{l}_y = i\hbar\left(-\cos\varphi\dfrac{\partial}{\partial\theta} + \cot\theta\sin\varphi\dfrac{\partial}{\partial\varphi}\right) \\ \hat{l}_z = -i\hbar\dfrac{\partial}{\partial\varphi} \end{cases}$$

总角动量平方

$$\hat{l}^2 = \hat{l}_x^2 + \hat{l}_y^2 + \hat{l}_z^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]$$

1，轨道角动量算符

- 例：验证$\psi_1(\boldsymbol{r})$、$\psi_2(\boldsymbol{r})$、$\psi_3(\boldsymbol{r})$分别为$\hat{l}_x$、$\hat{l}_y$、$\hat{l}_z$的本征态矢

$$\begin{cases} \psi_1(r,\theta,\varphi) = R(r)\sin\theta\cos\varphi \\ \psi_2(r,\theta,\varphi) = R(r)\sin\theta\sin\varphi \\ \psi_3(r,\theta,\varphi) = -R(r)\cos\theta \end{cases}$$

[解] $\hat{l}_x\psi_1(r,\theta,\varphi) = i\hbar(\sin\varphi\frac{\partial}{\partial\theta} + \cot\theta\cos\varphi\frac{\partial}{\partial\varphi})R(r)\sin\theta\cos\varphi$

$= i\hbar R(r)\,(\sin\varphi\cos\theta\cos\varphi - \cot\theta\cos\varphi\sin\theta\sin\varphi) = 0\times\psi_1$

$\hat{l}_y\psi_2(r,\theta,\varphi) = i\hbar(-\cos\varphi\frac{\partial}{\partial\theta} + \cot\theta\sin\varphi\frac{\partial}{\partial\varphi})R(r)\sin\theta\sin\varphi$

$= i\hbar R(r)\,(-\cos\varphi\cos\theta\sin\varphi + \cot\theta\sin\varphi\sin\theta\cos\varphi) = 0\times\psi_2$

$\hat{l}_z\psi_3(r,\theta,\varphi) = -i\hbar\frac{\partial}{\partial\varphi}R(r)\cos\theta$

$= 0\times\psi_3$

2，角动量算符对易关系

计算对易关系：$[\hat{l}_x, \hat{l}_y]$

$$[\hat{x}, \hat{p}_x] = i\hbar$$

$$[\hat{l}_x, \hat{l}_y] = [y\hat{p}_z - z\hat{p}_y,\ z\hat{p}_x - x\hat{p}_z]$$

$$= [y\hat{p}_z, z\hat{p}_x] - [y\hat{p}_z, x\hat{p}_z] - [z\hat{p}_y, z\hat{p}_x] + [z\hat{p}_y, x\hat{p}_z]$$

$$= -\, i\hbar y\hat{p}_x - 0 - 0 + i\hbar x\hat{p}_y = i\hbar(x\hat{p}_y - y\hat{p}_x) = i\hbar\hat{l}_z$$

同理可以证明：$[\hat{l}_y, \hat{l}_z] = i\hbar\hat{l}_x$， $[\hat{l}_z, \hat{l}_x] = i\hbar\hat{l}_y$

一般性地写作 $\boxed{[\hat{l}_i, \hat{l}_j] = i\hbar\varepsilon_{ijk}\hat{l}_k}$

可看作一种代数运算

$\varepsilon_{ijk} = 1$（ijk正排列）

$= -1$（kji正排列）

$= 0$（其它）

或：$\boxed{\hat{\boldsymbol{l}} \times \hat{\boldsymbol{l}} = i\hbar\hat{\boldsymbol{l}}}$

$$\hat{\vec{l}} \times \hat{\vec{l}} = \begin{vmatrix} \vec{e}_x & \vec{e}_y & \vec{e}_z \\ \hat{l}_x & \hat{l}_y & \hat{l}_z \\ \hat{l}_x & \hat{l}_y & \hat{l}_z \end{vmatrix} = \{[\hat{l}_y, \hat{l}_z], [\hat{l}_z, \hat{l}_x], [\hat{l}_x, \hat{l}_y]\} = i\hbar\{\hat{l}_x, \hat{l}_y, \hat{l}_z\}$$

2，角动量算符对易关系

计算对易关系： $[\hat{l}^2, \hat{l}_z]$

$$[\hat{l}^2, \hat{l}_z] = [\hat{l}_x{}^2, \hat{l}_z] + [\hat{l}_y{}^2, \hat{l}_z] + [\hat{l}_z{}^2, \hat{l}_z]$$

$$= \hat{l}_x [\hat{l}_x, \hat{l}_z] + [\hat{l}_x, \hat{l}_z] \hat{l}_x + \hat{l}_y [\hat{l}_y, \hat{l}_z] + [\hat{l}_y, \hat{l}_z] \hat{l}_y + 0$$

$$= - i\hbar \hat{l}_x \hat{l}_y - i\hbar \hat{l}_y \hat{l}_x + i\hbar \hat{l}_y \hat{l}_x + i\hbar \hat{l}_x \hat{l}_y = 0$$

同理可以证明： $[\hat{l}^2, \hat{l}_x] = 0$， $[\hat{l}^2, \hat{l}_y] = 0$

⇓

$\hat{l}^2$与$\hat{l}_z$（或$\hat{l}_x$、$\hat{l}_y$）具有共同的本征态矢集合

这些本征态矢集合是什么呢？

3，轨道角动量算符本征态矢

为对比起见，先计算动量算符$\hat{p}_x = -i\hbar\partial/\partial x$本征态矢：

设本征矢为$|\psi(x)>$，相应本征值为$\hbar k$，则**本征方程**为

$\hat{p}_x|\psi(x)> = \hbar k|\psi(x)>$，或：$-i\hbar\dfrac{\partial\psi}{\partial x} = \hbar k\psi$

解之：$$\frac{\partial\psi}{\psi} = ik\partial x \Rightarrow \ln\psi = ikx + \ln A \Rightarrow \psi(x) = Ae^{ikx}$$

它正是平面波的波函数！

可见k可以连续取值，因此$\hat{p}_x$的本征态矢集合$\{Ae^{ikx}\}$中的元素是**不可数无穷**的。

3，轨道角动量算符本征态矢

$\hat{l}_z = -i\hbar\partial/\partial\varphi$本征态矢的计算：

设本征矢为$|\psi_m(\varphi)>$，相应的本征值为$m\hbar$，解本征方程

$$\hat{l}_z|\psi_m(\varphi)> = m\hbar|\psi_m(\varphi)>，\text{或：} -i\hbar\frac{\partial\psi}{\partial\varphi} = m\hbar\psi$$

$$\text{解之：} \frac{\partial\psi}{\psi} = im\partial\varphi \Rightarrow \ln\psi = im\varphi + \ln A \Rightarrow \boxed{\psi(\varphi) = Ae^{im\varphi}}$$

归一化：$\int\psi^*\psi\mathrm{d}\varphi = 1 \Rightarrow A = (2\pi)^{-1/2}$

波函数的**单值性**要求：　$\psi(\varphi) = \psi(\varphi + 2\pi)$

$$Ae^{im\varphi} = Ae^{im(\varphi+2\pi)} \Rightarrow e^{i2\pi m} = 1 \Rightarrow \boxed{m = 0, \pm1, \pm2, \pm3, \ldots}$$

m是量子化的，称为**磁量子数**。

本征态矢集合$\{Ae^{im\varphi}\}$中元素是**可数**的！（会**无穷？**）

3，轨道角动量算符本征态矢

$\hat{l}^2$算符的本征态矢：

一般讨论$\hat{l}^2$与$\hat{l}_z$所具有共同本征态矢，记为$|\psi_{lm}(\theta,\varphi)>$；

本征方程：$\boxed{\hat{l}^2|\psi_{lm}(\theta,\varphi)> = \ ? \ |\psi_{lm}(\theta,\varphi)>}$。

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

数学上可以求出$\hat{l}^2$本征态矢及相应本征值：

连带Legendre函数

$$\psi(\theta,\varphi) = \mathrm{Y}_{lm}(\theta,\varphi) = \sqrt{\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}}\mathrm{P}_l^m(\cos\theta)e^{im\varphi}$$

球谐函数

$\hat{l}^2$本征值$l(l+1)\hbar^2$；故：$\boxed{\hat{l}^2|\psi_{lm}(\theta,\varphi)> = l(l+1)\hbar^2|\psi_{lm}(\theta,\varphi)>}$

3，轨道角动量算符本征态矢

为满足波函数物理条件，本征值也不能连续取值，表现在l和m只能如下取值：

$$\boxed{l = 0,\ 1,\ 2,\ 3,\ \ldots;\ \ m = 0,\ \pm1,\ \pm2,\ \pm3,\ \ldots,\ \pm l}$$

l称为**轨道量子数**，集合$\{Y_{lm}(\theta,\varphi)\}$元素最多为**可数无穷**。

易知：$\hat{l}_z|\psi_m(\varphi)> = m\hbar|\psi_m(\varphi)>$ （m取有限值）

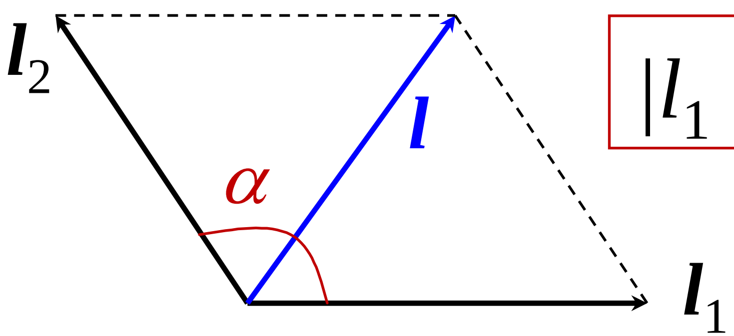
- 为书写方便，将本征矢$Y_{lm}(\theta,\varphi)$记为$|lm>$，且记$\hat{l} = (\hat{l}^2)^{1/2}$

$$\boxed{\begin{aligned}\hat{l}^2\,|lm> &= \hbar^2 l(l+1)\,|lm> \\ \hat{l}_z\,|lm> &= \hbar m\,|lm>\end{aligned}}$$

4，角动量合成的法则

- **经典力学中角动量合成：平行四边形法则**

合成角动量矢量$\boldsymbol{l} = \boldsymbol{l}_1 + \boldsymbol{l}_2$依赖于$|\boldsymbol{l}_1|$、$|\boldsymbol{l}_2|$及夹角$\alpha$：



$$\boxed{|l_1 - l_2|\,(\alpha = \pi) \le l \le l_1 + l_2\,(\alpha = 0)}$$

$l(\alpha)$是**连续函数**

- **量子力学中角动量合成法则（不证明）：**

总角动量$\boldsymbol{l} = \boldsymbol{l}_1 + \boldsymbol{l}_2$，算符$\hat{\boldsymbol{l}} = \hat{\boldsymbol{l}}_1 + \hat{\boldsymbol{l}}_2$。

若$\hat{\boldsymbol{l}}_1$、$\hat{\boldsymbol{l}}_2$本征矢分别为$|l_1 m_1>$和$|l_2 m_2>$，则可以证明：

$$\boxed{\begin{aligned} &\hat{l}^2 \,|\, lm> = \hbar^2 l(l+1)\,|\, lm>, \\ &l = l_1 + l_2, l_1 + l_2 - 1, l_1 + l_2 - 2, \ldots, |l_1 - l_2| \end{aligned}}$$

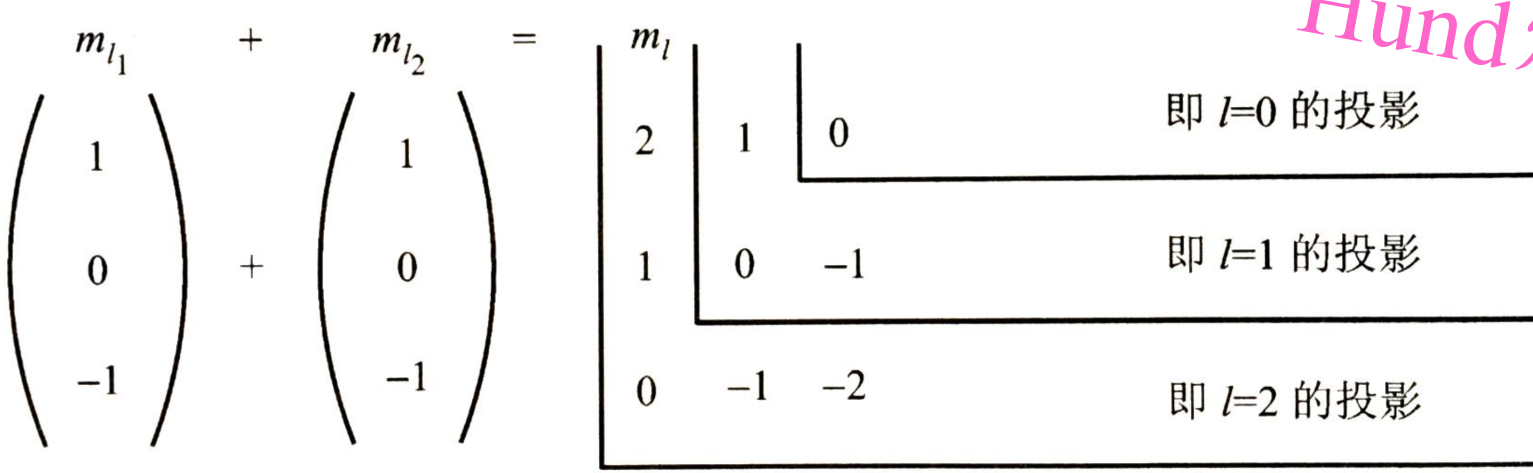
l是不连续的

4，角动量合成的法则

- **量子力学角动量合成一例**

设两个电子的轨道角动量分别为$\boldsymbol{l}_1$和$\boldsymbol{l}_2$，相应的角动量量子数为$l_1 = l_2 = 1$，故在z方向投影的量子数m_{l1}、m_{l2}均可取{1,0,-1}之一。这俩电子总轨道角动量$\boldsymbol{l} = \boldsymbol{l}_1 + \boldsymbol{l}_2$，其在第三方向$z$投影的量子数$m_l$的可能取值如下：

Hund定则



易见，总轨道角动量$\boldsymbol{l}$的量子数l可取{2,1,0}之一。

4，角动量合成的法则

- 例：有两个电子在中心力场中运动；它们的轨道角动量大小分别为$\sqrt{6}\hbar$和$\sqrt{30}\hbar$. 试分别以|*lm*>形式写出这两个电子的可能量子态，并写出双电子系统的量子态.

[解] $l_1 = 2,\ l_2 = 5;$

$m_1 = 0,\ \pm 1,\ \pm 2$（$2l_1 + 1 = 5$种）

$m_2 = 0,\ \pm 1,\ \pm 2,\ \pm 3,\ \pm 4,\ \pm 5$（$2l_2 + 1 = 11$种）

共$5\times 11 = 55$种可能合成方式

总角动量量子数：$l = \mathbf{7}\ (m = 0,\ \pm 1,\ \pm 2,\ \pm 3,\ \pm 4,\ \pm 5,\ \pm 6,\ \pm 7)$, 15

$\mathbf{6}\ (m = 0,\ \pm 1,\ \pm 2,\ \pm 3,\ \pm 4,\ \pm 5,\ \pm 6)$, 13

$\mathbf{5}\ (m = 0,\ \pm 1,\ \pm 2,\ \pm 3,\ \pm 4,\ \pm 5)$, 11

15+13+11+9+7=55

$\mathbf{4}\ (m = 0,\ \pm 1,\ \pm 2,\ \pm 3,\ \pm 4)$, $\mathbf{3}\ (m = 0,\ \pm 1,\ \pm 2,\ \pm 3)$

9 7

4，角动量合成的法则

将这55种量子态写出：

- 合成前

$|l_1 m_1>$：$|20>, |2\pm1>, |2\pm2>,$

$|l_2 m_2>$：$|50>, |5\pm1>, |5\pm2>, |5\pm3>, |5\pm4>, |5\pm5>$

- 合成后$|lm>$：

$|70>, |7\pm1>, |7\pm2>, |7\pm3>, |7\pm4>, |7\pm5>, |7\pm6>, |7\pm7>;$

$|60>, |6\pm1>, |6\pm2>, |6\pm3>, |6\pm4>, |6\pm5>, |6\pm6>;$

$|50>, |5\pm1>, |5\pm2>, |5\pm3>, |5\pm4>, |5\pm5>;$

$|40>, |4\pm1>, |4\pm2>, |4\pm3>, |4\pm4>;$

$|30>, |3\pm1>, |3\pm2>, |3\pm3>.$

总 结

1，轨道角动量算符

2，角动量算符对易关系

3，轨道角动量算符本征态矢

4，角动量合成的法则

作　业

1, 数学中有个大家熟悉的恒等式 $(a+b)(a-b)=a^2-b^2$。在量子力学中 a、b 成为算符 $\hat{a}$ 和 $\hat{b}$，上式仍普遍成立吗？

2, 证明 $\hat{\boldsymbol{p}} \times \hat{\boldsymbol{l}} + \hat{\boldsymbol{l}} \times \hat{\boldsymbol{p}} = 2i\hbar\hat{\boldsymbol{p}}$.