第5章、 氢原子量子理论

- 氢原子的量子行为
- 量子纠缠

5.1.1 角动量算符

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

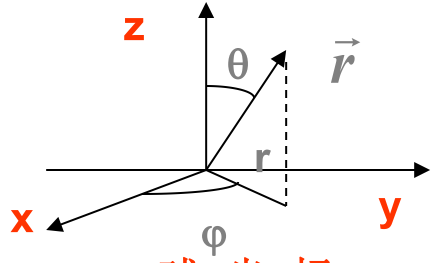
$$\text{直角坐标系} \rightarrow \begin{cases} L_x = y\hat{p}_z - z\hat{p}_y = -i\hbar(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}) \\ L_y = z\hat{p}_x - x\hat{p}_z = -i\hbar(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}) \\ L_z = x\hat{p}_y - y\hat{p}_x = -i\hbar(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}) \end{cases}$$

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

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

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

$$\rightarrow\begin{cases} x = r\sin\theta\cos\varphi \\ y = r\sin\theta\sin\varphi \\ z = r\cos\theta \end{cases} \quad \begin{cases} r^2 = x^2 + y^2 + z^2 & (1) \\ \cos\theta = z/r & (2) \\ \tan\varphi = y/x & (3) \end{cases}$$



球 坐 标

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

利用 $\rightarrow \dfrac{\partial f}{\partial x_i} = \dfrac{\partial f}{\partial r}\dfrac{\partial r}{\partial x_i} + \dfrac{\partial f}{\partial \theta}\dfrac{\partial \theta}{\partial x_i} + \dfrac{\partial f}{\partial \varphi}\dfrac{\partial \varphi}{\partial x_i} \rightarrow \begin{cases} \dfrac{\partial}{\partial x} = \dfrac{\partial}{\partial r}\dfrac{\partial r}{\partial x} + \dfrac{\partial}{\partial \theta}\dfrac{\partial \theta}{\partial x} + \dfrac{\partial}{\partial \varphi}\dfrac{\partial \varphi}{\partial x} \\ \dfrac{\partial}{\partial y} = \dfrac{\partial}{\partial r}\dfrac{\partial r}{\partial y} + \dfrac{\partial}{\partial \theta}\dfrac{\partial \theta}{\partial y} + \dfrac{\partial}{\partial \varphi}\dfrac{\partial \varphi}{\partial y} \\ \dfrac{\partial}{\partial z} = \dfrac{\partial}{\partial r}\dfrac{\partial r}{\partial z} + \dfrac{\partial}{\partial \theta}\dfrac{\partial \theta}{\partial z} + \dfrac{\partial}{\partial \varphi}\dfrac{\partial \varphi}{\partial z} \end{cases}$

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

则角动量算符在球坐标中的 表达式为：

$$
由\begin{cases}
L_x=y\hat{p}_z-z\hat{p}_y=-i\hbar(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y})\\
L_y=z\hat{p}_x-x\hat{p}_z=-i\hbar(z\frac{\partial}{\partial x}-x\frac{\partial}{\partial z})\\
L_z=x\hat{p}_y-y\hat{p}_x=-i\hbar(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x})
\end{cases}
\rightarrow
\begin{cases}
\hat{L}_x=i\hbar[\sin\varphi\dfrac{\partial}{\partial\theta}+\cot\theta\cos\varphi\dfrac{\partial}{\partial\varphi}]\\
\hat{L}_y=-i\hbar[\cos\varphi\dfrac{\partial}{\partial\theta}+\cot\theta\sin\varphi\dfrac{\partial}{\partial\varphi}]\\
\hat{L}_z=-i\hbar\dfrac{\partial}{\partial\varphi}
\end{cases}
$$

$$
\hat{L}^2=-\hbar^2[(y\tfrac{\partial}{\partial z}-z\tfrac{\partial}{\partial y})^2+(z\tfrac{\partial}{\partial x}-x\tfrac{\partial}{\partial z})^2+(x\tfrac{\partial}{\partial y}-y\tfrac{\partial}{\partial x})^2\rightarrow
$$

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

5.1.2 氢原子中电子角动量的量子化

1：氢原子周围电子角动量方向：磁量子数

$$\begin{cases} \hat{L}_x = i\hbar[\sin\varphi\frac{\partial}{\partial\theta} + \cot\theta\cos\varphi\frac{\partial}{\partial\varphi}] \\ \hat{L}_y = -i\hbar[\cos\varphi\frac{\partial}{\partial\theta} + \cot\theta\sin\varphi\frac{\partial}{\partial\varphi}] \\ \hat{L}_z = -i\hbar\frac{\partial}{\partial\varphi} \end{cases} \rightarrow \quad \hat{L}_z = -i\hbar\frac{\partial\psi}{\partial\varphi} = L_z\psi \quad \rightarrow \psi = Ae^{im\varphi} \quad m = \frac{L_z}{\hbar}$$

波函数单值条件，要求当 φ 转过 2π 角回到原位时波函数值相等，即：

$$\psi(\varphi) = \psi(\varphi+2\pi) \rightarrow Ae^{im\varphi} = Ae^{im(\varphi+2\pi)}$$

$m = 0, \pm1, \pm2, \cdots$ 定义为磁量子数

$$\rightarrow L_z = m\hbar \qquad m = 0, \pm1, \pm2, \cdots$$

求归一化系数

$$\int_0^{2\pi} |\psi|^2 \, d\varphi = A^2 \int_0^{2\pi} d\varphi = 2\pi c^2 = 1 \rightarrow A = \frac{1}{\sqrt{2\pi}} \qquad \psi(\varphi) = \frac{1}{\sqrt{2\pi}} e^{im\varphi} \qquad m = \frac{L_z}{\hbar}$$

正交性：

$$\frac{1}{2\pi} \int_0^{2\pi} e^{-im\varphi} e^{in\varphi} d\varphi = 0 \qquad (n \neq m)$$

合记之得正交归一化 条件：

$$\frac{1}{2\pi} \int_0^{2\pi} e^{-im\varphi} e^{in\varphi} d\varphi = \delta_{mn}$$

2：氢原子周围电子角动量的大小：L²的本征值问题

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

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

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

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

两边同时相乘 $\dfrac{\sin^2\theta}{\Theta(\theta)\Phi(\varphi)}$

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

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

$$\rightarrow\begin{cases}\dfrac{\sin\theta}{\Theta(\theta)}\dfrac{d}{d\theta}\left(\sin\theta\dfrac{d\Theta}{d\theta}\right)+\lambda\sin^2\theta=m^2\\ \dfrac{d^2\Phi(\varphi)}{d\varphi^2}=-m^2\Phi(\varphi)\end{cases}$$

$$\rightarrow\begin{cases}\dfrac{1}{\sin\theta}\dfrac{d}{d\theta}\left(\sin\theta\dfrac{d\Theta}{d\theta}\right)+\left(\lambda-\dfrac{m^2}{\sin^2\theta}\right)\Theta(\theta)=0\\ \dfrac{d^2\Phi(\varphi)}{d\varphi^2}+m^2\Phi(\varphi)=0\end{cases}$$

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

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

上 面 方 程 有 解 的 必 要 条 件： $\lambda = l(l+1)$

$\lambda=\frac{L^2}{\hbar^2}\rightarrow L=\sqrt{l(l+1)}\hbar$　　$l=0,1,2,3...$定义为角动量子数

磁 量 子 数： $m = 0,\pm 1,\pm 2,\cdots l$

$$L^2 Y_{lm} = l(l+1)\hbar^2 Y_{lm}$$

球谐函数

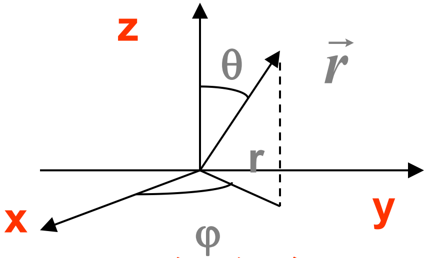
$$l=0 \to Y_{00} = \frac{1}{\sqrt{4\pi}} \quad l=1 \to \begin{cases} Y_{11} = -\sqrt{\dfrac{3}{8\pi}} \sin\theta e^{i\phi} \\ Y_{10} = \sqrt{\dfrac{3}{4\pi}} = \cos\theta \\ Y_{1-1} = \sqrt{\dfrac{3}{8\pi}} \sin\theta e^{-i\phi} \end{cases}$$

$$\to \begin{cases} Y_{00} = \dfrac{1}{\sqrt{4\pi}} \\ Y_{1,1} = \dfrac{3}{\sqrt{8\pi}} \sin\theta e^{i\phi} \\ Y_{1,0} = \dfrac{3}{\sqrt{4\pi}} \cos\theta \\ Y_{1,-1} = \dfrac{3}{\sqrt{8\pi}} \sin\theta e^{-i\phi} \end{cases}$$

3.氢原子的能级

体系 Hamilton 量

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}$$



球 坐 标

$$\rightarrow \left[-\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r} \right]\psi = E\psi$$

$$\rightarrow -\frac{\hbar^2}{2\mu}\left(\frac{1}{r^2}\right)\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \right]\psi - \frac{Ze^2}{4\pi\varepsilon_0 r}\psi = E\psi$$

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

$$\rightarrow \left[-\frac{\hbar^2}{2\mu r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\hat{L}^2}{2\mu r^2} - \frac{Ze^2}{4\pi\varepsilon_0 r} \right]\psi = E\psi$$

$$\rightarrow\left[-\frac{\hbar^2}{2\mu r^2}\frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r})+\frac{\hat{L}^2}{2\mu r^2}-\frac{Ze^2}{4\pi\varepsilon_0 r}\right]\psi=E\psi$$

$$\rightarrow-\frac{\hbar^2}{2\mu r^2}\left[\frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r})+\frac{\hat{L}^2}{2\mu r^2}-\frac{Ze^2}{4\pi\varepsilon_0 r}\right]R(r)Y_{lm}(\theta,\varphi)=ER(r)Y_{lm}(\theta,\varphi)$$

$$L^2Y\left(l,m\right)=l\left(l+1\right)\hbar^2Y\left(l,m\right)$$

令 R(r) = u(r)/r代入上式得：

$$\frac{d^2u}{dr^2}+\left[\frac{2\mu_{\text{电子质量}}}{\hbar^2}\left(E+\frac{Ze^2}{4\pi\varepsilon_0 r}\right)-\frac{l(l+1)}{r^2}\right]u=0$$

令$U(r)=\frac{l(l+1)\hbar^2}{2\mu r^2}-\frac{Ze^2}{4\pi\varepsilon_0 r}\rightarrow\frac{d^2u}{dr^2}+\frac{2\mu}{\hbar^2}[E-U(r)]u=0$

$$\rightarrow \frac{d^2u}{dr^2}+\frac{2\mu}{\hbar^2}[E-U(r)]u=0$$

讨论 E < 0 情况，方程可改写如下：

$$\rightarrow \frac{d^2u}{dr^2}+\left[\frac{2\mu}{\hbar^2}\frac{Ze^2}{4\pi\varepsilon_0 r}-\frac{2\mu}{\hbar^2}|E|-\frac{l(l+1)}{r^2}\right]u=0$$ 最后解出： $$E_n=-\frac{\mu Z^2e^4}{2\hbar^2n^2}\rightarrow n=1,2,3\cdots$$

波尔半径的求解

试探解： $u(r)=rAe^{-\frac{Zr}{a_0}}$

波尔半径：角动量为0时的临界半径

$$\frac{d^2u(r)}{dr^2}=-\frac{2ZA}{a_0}e^{-\frac{Zr}{a_0}}+\frac{Z^2r}{a_0^2}Ae^{-\frac{Zr}{a_0}}\rightarrow \frac{d^2u}{dr^2}+\left[\frac{2\mu}{\hbar^2}\frac{Ze^2}{4\pi\varepsilon_0 r}-\frac{2\mu}{\hbar^2}|E|-\frac{l(l+1)}{r^2}\right]u=0$$

$$\rightarrow \frac{z^2}{a_0^2}-\frac{2\mu}{\hbar^2}|E|+\frac{2\mu}{\hbar^2}\frac{Ze^2}{4\pi\varepsilon_0 r}-\frac{2Z}{ra_0}-\frac{l(l+1)}{r^2}=0$$

$$\rightarrow \frac{z^2}{a_0^2} - \frac{2\mu}{\hbar^2}|E| + \frac{2\mu}{\hbar^2}\frac{Ze^2}{4\pi\varepsilon_0 r} - \frac{2z}{ra_0} - \frac{l(l+1)}{r^2} = 0$$

$$\rightarrow \frac{2\mu}{\hbar^2}\frac{Ze^2}{4\pi\varepsilon_0 r} - \frac{2z}{ra_0} = 0 \quad \rightarrow a_0 = \frac{4\pi\varepsilon_0\hbar^2}{\mu e^2}$$

波尔半径为：$\mathrm{a}_{01} = 0.0529\mathrm{nm}$

波尔半径对应的最小能量

同时 $\rightarrow \frac{z^2}{a_0^2} - \frac{2\mu}{\hbar^2}|E| = 0 \rightarrow E_{\text{波尔半径的最小能量}} = -\frac{\hbar^2 z^2}{2\mu a_0^2}$

$$E_{\text{波尔半径的最小能量}} = -\frac{\hbar^2 z^2}{2\mu a_0^2} = \frac{\mu e^4 z^2}{32\pi^2\varepsilon_0^2\hbar^2}$$

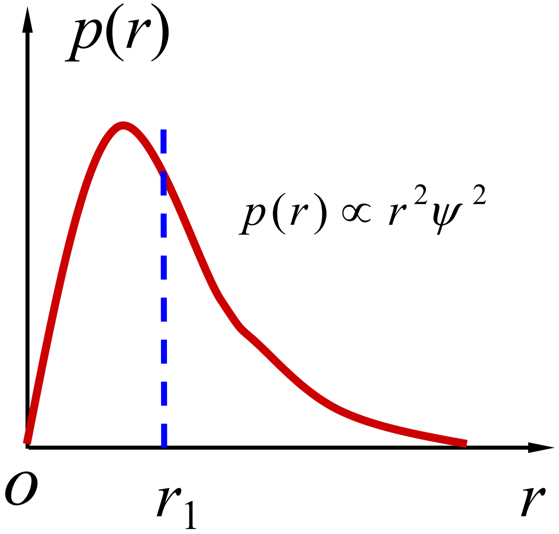
径向波函数

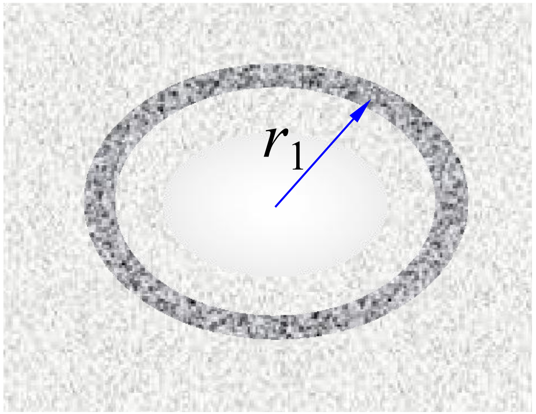
$$R_{nl}(r)=N_{nl}e^{-\frac{Z}{a_0 n}r}\left(\frac{2Z}{a_0 n}r\right)^{l}L_{n+l}^{2l+1}\left(\frac{2Z}{a_0 n}r\right)\rightarrow\begin{cases}R_{10}(r)=\left(\frac{Z}{a_0}\right)^{3/2}2e^{-\frac{Z}{a_0}r}\\ R_{20}(r)=\left(\frac{Z}{2a_0}\right)^{3/2}(2-\frac{Z}{a_0}r)e^{-\frac{Z}{2a_0}r}\\ R_{21}(r)=\left(\frac{Z}{2a_0}\right)^{3/2}\frac{Z}{a_0\sqrt{3}}re^{-\frac{Z}{2a_0}r}\\ R_{30}(r)=\left(\frac{Z}{3a_0}\right)^{3/2}[2-\frac{4Z}{3a_0}r+\frac{4}{27}(\frac{Z}{a_0}r)^2]e^{-\frac{Z}{3a_0}r}\\ R_{31}(r)=\left(\frac{2Z}{a_0}\right)^{3/2}[\frac{2}{27\sqrt{3}}-\frac{Z}{81\sqrt{3}a_0}r]\frac{Z}{a_0}re^{-\frac{Z}{3a_0}r}\\ R_{31}(r)=\left(\frac{2Z}{a_0}\right)^{3/2}\frac{Z}{81\sqrt{15}}(\frac{Z}{a_0}r)^2e^{-\frac{Z}{3a_0}r}\end{cases}$$

波尔半径为：$a_{01}=\dfrac{\varepsilon_0 h^2}{\pi m e^2}=0.0529\text{nm}$

总波函数 $\rightarrow \psi_{nlm}(r,\theta,\phi)=R_{nl}(r)Y_{lm}(\theta,\phi)$

●电子的分布概率

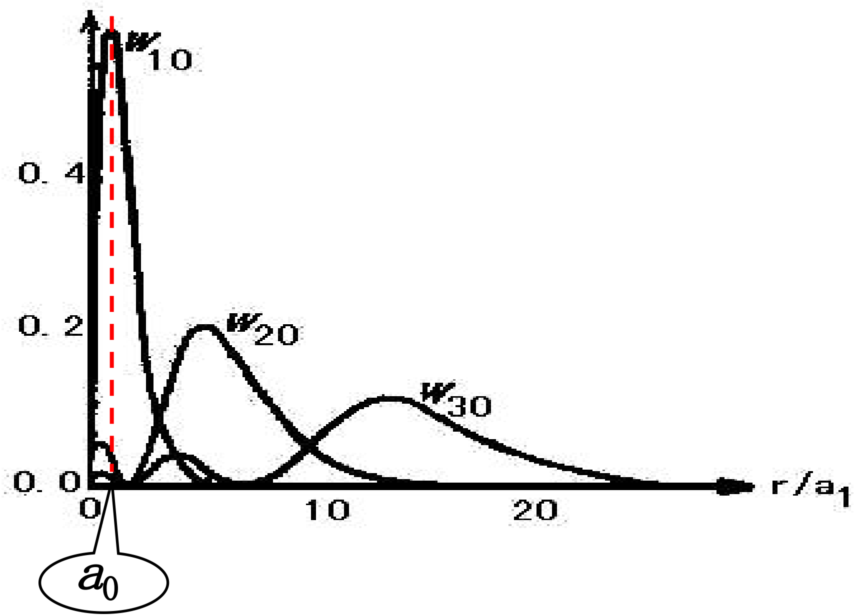




电子云

电子沿径向的几率分布是连续的——不同于经典的轨道概念。

在基态，电子在$r=a_0$处出现的几率最大，与经典轨道对应。



4. 电子的自旋算符和自旋波函数

●自旋角动量

$$
轨道角动量算符:\begin{cases}\hat{L}_x\hat{L}_y-\hat{L}_y\hat{L}_x=i\hbar\hat{L}_z\\ \hat{L}_y\hat{L}_z-\hat{L}_z\hat{L}_y=i\hbar\hat{L}_x\\ \hat{L}_z\hat{L}_x-\hat{L}_x\hat{L}_z=i\hbar\hat{L}_y\\ \hat{L}_2=\hat{L}_x^2+\hat{L}_y^2+\hat{L}_z^2\end{cases}\rightarrow 自旋角动量\begin{cases}\hat{S}_x\hat{S}_y-\hat{S}_y\hat{S}_x=i\hbar\hat{S}_z\\ \hat{S}_y\hat{S}_z-\hat{S}_z\hat{S}_y=i\hbar\hat{S}_x\\ \hat{S}_z\hat{S}_x-\hat{S}_x\hat{S}_z=i\hbar\hat{S}_y\\ \hat{S}=\hat{S}_x^2+\hat{S}_y^2+\hat{S}_z^2\end{cases}
$$

$$
自旋角动量\rightarrow\begin{cases}\hat{S}^2\hat{S}_x-\hat{S}_x\hat{S}^2=0\\ \hat{S}^2\hat{S}_y-\hat{S}_y\hat{S}^2=0\\ \hat{S}^2\hat{S}_z-\hat{S}_z\hat{S}^2=0\end{cases}
$$

$$
构建算符:\begin{cases}\hat{A}(算符)=\hat{S}_x+i\hat{S}_y\\ \hat{B}(算符)=\hat{S}_x-i\hat{S}_y\end{cases}
$$

$$
\rightarrow\begin{cases}\hat{A}\hat{B}=\left(\hat{S}_x+i\hat{S}_y\right)\left(\hat{S}_x-i\hat{S}_y\right)=\hat{S}_x^2+\hat{S}_y^2+i\left(\hat{S}_y\hat{S}_x-\hat{S}_x\hat{S}_y\right)=\hat{S}_x^2+\hat{S}_y^2+\hbar\hat{S}_z\\ \hat{B}\hat{A}=\left(\hat{S}_x-i\hat{S}_y\right)\left(\hat{S}_x+i\hat{S}_y\right)=\hat{S}_x^2+\hat{S}_y^2-i\left(\hat{S}_y\hat{S}_x-\hat{S}_x\hat{S}_y\right)=\hat{S}_x^2+\hat{S}_y^2-\hbar\hat{S}_z\end{cases}
$$

$$\rightarrow \begin{cases} \hat{A}\hat{B} = \hat{S}_x^2 + \hat{S}_y^2 + \hbar S_z \\ \hat{B}\hat{A} = \hat{S}_x^2 + \hat{S}_y^2 - \hbar \hat{S}_z \end{cases} \rightarrow \begin{cases} \hat{A}\hat{B} = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 - \hat{S}_z^2 + \hbar S_z = \hat{S}^2 - \hat{S}_z^2 + \hbar \hat{S}_z \\ \hat{B}\hat{A} = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 - \hat{S}_z^2 - \hbar \hat{S}_z = \hat{S}^2 - \hat{S}_z^2 - \hbar \hat{S}_z \end{cases}$$

$$\rightarrow \begin{cases} \hat{A}\hat{S}_z = \left(\hat{S}_x + i\hat{S}_y\right)\hat{S}_z = \hat{S}_x\hat{S}_z + i\hat{S}_y\hat{S}_z = \hat{S}_z\hat{A} - \hbar\hat{A} = \left(\hat{S}_z - \hbar\right)\hat{A} \\ \hat{B}\hat{S}_z = \left(\hat{S}_x - i\hat{S}_y\right)\hat{S}_z = \hat{S}_x\hat{S}_z - i\hat{S}_y\hat{S}_z + \hbar\hat{S}_x - \hbar\hat{S}_x = \left(\hat{S}_z + \hbar\right)\hat{B} \end{cases}$$

$\hat{S}^2$与$\hat{S}_z$对易，有共同的本征函数 $\rightarrow \begin{cases} \hat{S}^2\Phi = c\Phi \\ \hat{S}_z\Phi = b\Phi \end{cases} \rightarrow S^2 = c, S_z = b$

$$\hat{A}\hat{S}_z\Phi = \hat{A}b\Phi \rightarrow \left(\hat{S}_z\hat{A} - \hbar\hat{A}\right)\Phi = \hat{A}b\Phi \rightarrow \hat{S}_z\left(\hat{A}\Phi\right) = \left(b + \hbar\right)\hat{A}\Phi$$

$\hat{A}\Phi$是本征函数，其本征值为$(b+\hbar)$，即$\hat{S}_z$的本征函数被$\hat{A}$作用后，仍然是它的本征函数, 但本征值增加了

$$\hat{A}\left[\hat{S}_z\left(\hat{A}\Phi\right)\right] \rightarrow \hat{S}_z\left(\hat{A}^2\Phi\right) = \left(b + 2\hbar\right)\hat{A}^2\Phi \rightarrow \hat{S}_z\left(\hat{A}^k\Phi\right) = \left(b + k\hbar\right)\hat{A}^k\Phi$$

同理：$\hat{S}_z\left(\hat{B}^k\Phi\right)=\left(b-k\hbar\right)\hat{B}^k\Phi$

$$\begin{cases}\hat{S}_z\left(\hat{A}^k\Phi\right)=\left(b+k\hbar\right)\hat{A}^k\Phi\\ \hat{S}_z\left(\hat{B}^k\Phi\right)=\left(b-k\hbar\right)\hat{B}^k\Phi\end{cases}\rightarrow k=0,1,2,3,4\ldots$$

$\hat{S}_z$的本征值是. . . , $b+2\hbar,b+\hbar,b,b-\hbar,b-2\hbar\ldots$

$$\text{观察：}\begin{cases}\hat{S}^2\hat{A}-\hat{A}\hat{S}^2=\hat{S}^2\left(\hat{S}_x+i\hat{S}_y\right)-\left(\hat{S}_x+i\hat{S}_y\right)\hat{S}^2=\left(\hat{S}^2\hat{S}_x-\hat{S}_x\hat{S}^2\right)+i\left(\hat{S}^2\hat{S}_y-\hat{S}_y\hat{S}^2\right)=0\\ \hat{S}^2\hat{B}-\hat{B}\hat{S}^2=\hat{S}^2\left(\hat{S}_x-i\hat{S}_y\right)-\left(\hat{S}_x-i\hat{S}_y\right)\hat{S}^2=\left(\hat{S}^2\hat{S}_x-\hat{S}_x\hat{S}^2\right)-i\left(\hat{S}^2\hat{S}_y-\hat{S}_y\hat{S}^2\right)=0\end{cases}$$

$\rightarrow\hat{S}^2$与$\hat{A}$或者$\hat{B}$对易$\rightarrow$它们有共同的本征值和本征函数

$$\text{观察：}\begin{cases}\hat{S}^2\hat{A}=\hat{A}\hat{S}^2\\ \hat{S}^2\hat{B}=\hat{B}\hat{S}^2\end{cases}\rightarrow\begin{cases}\hat{S}^2\hat{A}^2=\hat{A}\hat{S}^2\hat{A}=\hat{A}^2\hat{S}^2\\ \hat{S}^2\hat{B}^2=\hat{B}\hat{S}^2\hat{B}=\hat{B}^2\hat{S}^2\end{cases}\rightarrow\begin{cases}\hat{S}^2\hat{A}^k=\hat{A}^k\hat{S}^2\\ \hat{S}^2\hat{B}^k=\hat{B}^k\hat{S}^2\end{cases}$$

$$\rightarrow\begin{cases}\hat{S}^2\hat{A}^k\Phi=\hat{A}^k\hat{S}^2\Phi=\hat{A}^kc\Phi=c\hat{A}^k\Phi\\ \hat{S}^2\hat{B}^k\Phi=\hat{B}^k\hat{S}^2\Phi=\hat{B}^kc\Phi=c\hat{B}^k\Phi\end{cases}$$

$$\hat{S}_z\Phi = b\Phi \to \hat{S}_z\Phi_k = b_k\Phi_k,\text{式中}\ \Phi_k = A^k\left(B^k\right)\Phi, b_k = b \pm k\hbar$$

$$\hat{S}_z^2\Phi_k = b_k\hat{S}_z\Phi_k = b_k^2\Phi_k$$

$$\begin{cases} \hat{S}^2\hat{A}^k\Phi = \hat{A}^k\hat{S}^2\Phi = \hat{A}^k c\Phi = c\hat{A}^k\Phi \\ \hat{S}^2\hat{B}^k\Phi = \hat{B}^k\hat{S}^2\Phi = \hat{B}^k c\Phi = c\hat{B}^k\Phi \\ \hat{S}_z^2\Phi_k = b_k\hat{S}_z\Phi_k = b_k^2\Phi_k \end{cases} \to\to \begin{cases} \hat{S}^2\hat{A}^k\Phi - \hat{S}_z^2\Phi_k = c\hat{A}^k\Phi - b_k^2\Phi_k = c\Phi_k - b_k^2\Phi_k \\ \hat{S}^2\hat{B}^k\Phi - \hat{S}_z^2\Phi_k = c\hat{B}^k\Phi - b_k^2\Phi_k = c\Phi_{-k} - b_{-k}^2\Phi_{-k} \end{cases}$$

$$\hat{S} = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 \to \text{代入}\begin{cases} \hat{S}^2\hat{A}^k\Phi - \hat{S}_z^2\Phi_k = c\Phi_k - b_k^2\Phi_k \\ \hat{S}^2\hat{B}^k\Phi - \hat{S}_z^2\Phi_k = c\Phi_{-k} - b_{-k}^2\Phi_{-k} \end{cases} \text{得} \to \hat{S}_x^2 + \hat{S}_y^2 = c\Phi_k - b_k^2\Phi_k$$

$\hat{S}_x^2 + \hat{S}_y^2 = c\Phi_k - b_k^2\Phi_k = \left(c - b_k^2\right)\Phi_k \to \left(c - b_k^2\right)$是算符$\left(\hat{S}_x^2 + \hat{S}_y^2\right)$的本征值，此式中必须是正的

$\to -\sqrt{c} \le b_k \le \sqrt{c}$ $\qquad \to c$与k无关，说明$\hat{S}_z$的本征值有上下限

$\rightarrow -\sqrt{c} \le b_k \le \sqrt{c}$ $\rightarrow c$与k无关，说明$\hat{S}_z$的本征值有上下限

则必然有 $\rightarrow \begin{cases} \hat{S}_z \Phi_{\max} = b_{\max} \Phi_{\max} \\ \hat{S}_z \Phi_{\min} = b_{\min} \Phi_{\min} \end{cases} \rightarrow \begin{cases} \hat{A}\hat{S}_z \Phi_{\max} = b_{\max} \hat{A}\Phi_{\max} \\ \hat{B}\hat{S}_z \Phi_{\min} = b_{\min} \hat{B}\Phi_{\min} \end{cases}$

$$\begin{cases} \hat{A}\hat{S}_z = \left(\hat{S}_z - \hbar\right)\hat{A} \\ \hat{B}\hat{S}_z = \left(\hat{S}_z + \hbar\right)\hat{B} \end{cases} \rightarrow \text{代入} \begin{cases} \hat{A}\hat{S}_z \Phi_{\max} = b_{\max} \hat{A}\Phi_{\max} \\ \hat{B}\hat{S}_z \Phi_{\min} = b_{\min} \hat{B}\Phi_{\min} \end{cases} \rightarrow \text{得} \begin{cases} \left(\hat{S}_z - \hbar\right)\hat{A}\Phi_{\max} = b_{\max}\hat{A}\Phi_{\max}, \\ \left(\hat{S}_z + \hbar\right)\hat{B}\Phi_{\min} = b_{\min}\hat{B}\Phi_{\min}, \end{cases}$$

$$\begin{cases} \left(\hat{S}_z - \hbar\right)\hat{A}\Phi_{\max} = b_{\max}\hat{A}\Phi_{\max} \\ \left(\hat{S}_z + \hbar\right)\hat{B}\Phi_{\min} = b_{\min}\hat{B}\Phi_{\min} \end{cases} \rightarrow \begin{cases} \hat{S}_z\hat{A}\Phi_{\max} = \left(b_{\max} + \hbar\right)\hat{A}\Phi_{\max} \\ \hat{S}_z\hat{B}\Phi_{\min} = \left(b_{\min} - \hbar\right)\hat{B}\Phi_{\min} \end{cases}$$

$\hat{A}\Phi_{\max}\left(\hat{B}\Phi_{\min}\right)$都是$\hat{S}_z$的本征函数，对应的本征值$(b_{\max}+\hbar)$或者$(b_{\min}-\hbar)$，与最大值和最小值矛盾

$$\text{必有} \rightarrow \begin{cases} \hat{A}\Phi_{\max} = 0 \\ \hat{B}\Phi_{\min} = 0 \end{cases}$$

$$\begin{cases}\hat{A}\Phi_{max}=0\\ \hat{B}\Phi_{min}=0\end{cases}\rightarrow\begin{cases}\hat{B}\hat{A}\Phi_{max}=0\\ \hat{A}\hat{B}\Phi_{min}=0\end{cases}\rightarrow$$

$$\begin{cases}\hat{A}\hat{B}=\hat{S}^2-\hat{S}_z^2+\hbar S_z\\ \hat{B}\hat{A}=\hat{S}^2-\hat{S}_z^2-\hbar S_z\end{cases}\rightarrow \text{代入}\rightarrow\begin{cases}\hat{B}\hat{A}\Phi_{max}=0\\ \hat{A}\hat{B}\Phi_{min}=0\end{cases}\rightarrow\begin{cases}\left(\hat{S}^2-\hat{S}_z^2-\hbar S_z\right)\Phi_{max}=0\\ \left(\hat{S}^2-\hat{S}_z^2+\hbar S_z\right)\Phi_{min}=0\end{cases}$$

$$\rightarrow\begin{cases}c-b_{max}^2-\hbar b_{max}=0\\ c-b_{min}^2+\hbar b_{min}=0\end{cases}\rightarrow \text{相减得}-b_{min}^2+\hbar b_{min}+b_{max}^2+\hbar b_{max}=0$$

$$-b_{min}^2+\hbar b_{min}+b_{max}^2+\hbar b_{max}=0\rightarrow \text{只有这解}\, b_{max}=-b_{min}$$

$$\text{由}\, b_k=b\pm k\hbar\rightarrow b_{max}-b_{min}=n\hbar, n=0,1,2,3,4\ldots$$

此处的n可以取任意自然数是因为虽然b的最大与最小值互为相反数，但是两者对应的k不一定互为相反数，因为还要加上一个b！

$$\begin{cases}b_{max}-b_{min}=n\hbar\\ b_{max}=-b_{min}\end{cases}\rightarrow b_{max}=\frac{1}{2}n\hbar\rightarrow\begin{cases}b_{max}=j\hbar\\ b_{min}=-j\hbar\end{cases}, j=0,\frac{1}{2},1,\frac{3}{2}\ldots.$$

$$c-b_{max}^2-\hbar b_{max}=0\rightarrow c=b_{max}^2+\hbar b_{max}\leftarrow b_{max}=j\hbar\rightarrow \text{得}\, c=j\left(j+1\right)\hbar^2$$

由于c是$\hat{S}^2$的本征值，$\hat{S}^2$对应的物理量一定是S^2,所以$S^2=c=j(j+1)\hbar^2$

$$\to S=\sqrt{j(j+1)}\hbar$$

电子自旋角动量只能取$j=\frac{1}{2}\to S=\sqrt{j(j+1)}\hbar=\frac{\sqrt{3}}{2}\hbar$

同理，角动量$j=0,1,2,\ldots,\mathrm{n}-1\to L=\sqrt{j(j+1)}\hbar$

最后一项就是考虑了自旋方向之后的结果，并且电子的自旋只能取这两个之中的一个

●自旋波函数

$$\psi=\psi(x,y,z,S_z,t)\to\begin{cases}\psi_1(\vec{r},t)=\psi(x,y,z,+\frac{\hbar}{2},t)=\psi(\vec{r},t)\chi(\frac{\hbar}{2})\\ \psi_2(\vec{r},t)=\psi(x,y,z,-\frac{\hbar}{2},t)=\psi(\vec{r},t)\chi(-\frac{\hbar}{2})\end{cases}$$

$$\begin{cases}\psi_1(\vec{r},t)=\psi(\vec{r},t)\chi(\frac{\hbar}{2}) \\ \psi_2(\vec{r},t)=\psi(\vec{r},t)\chi(-\frac{\hbar}{2})\end{cases} \rightarrow \Phi=\begin{bmatrix}\psi_1(\vec{r},t)=\psi(\vec{r},t)\chi(\frac{\hbar}{2}) \\ \psi_2(\vec{r},t)=\psi(\vec{r},t)\chi(-\frac{\hbar}{2})\end{bmatrix}=\begin{bmatrix}\psi_1(\vec{r},t) \\ \psi_2(\vec{r},t)\end{bmatrix}$$

若已知电子处于$S_z = \hbar/2$或$S_z = -\hbar/2$的自旋态，则波函数可分别写为：

$$\Phi_{\frac{1}{2}}=\begin{bmatrix}\psi_1(\vec{r},t) \\ 0\end{bmatrix} \qquad \Phi_{-\frac{1}{2}}=\begin{bmatrix}0 \\ \psi_2(\vec{r},t)\end{bmatrix}$$

电子自旋算符（如S_Z）是作用与电子自旋波函数上的，既然电子波函数表示成了2×1 的列矩阵，那末，电子自旋算符的矩阵表示应该是 2×2 矩阵。

$$\hat{S}_z=\frac{\hbar}{2}\begin{bmatrix}a & b \\ c & d\end{bmatrix}$$

就是要注意，这个矩阵是作用于自旋波函数上面的，所以对应的本征值为(-)h/2.

因为$\Phi_{1/2}$描写的态，S_Z有确定值 $\hbar/2$，所以$\Phi_{1/2}$是 S_Z 的本征态，本征值为 $\hbar/2$，即有：

$$\hat{S}_z\Phi_{\frac{1}{2}}=\frac{\hbar}{2}\Phi_{\frac{1}{2}}\rightarrow\frac{\hbar}{2}\begin{bmatrix}a & b\\ c & d\end{bmatrix}\begin{bmatrix}\psi_1(\vec{r},t)\\ 0\end{bmatrix}=\frac{\hbar}{2}\begin{bmatrix}\psi_1(\vec{r},t)\\ 0\end{bmatrix}$$

$$\begin{bmatrix}a\psi_1\\ c\psi_1\end{bmatrix}=\begin{bmatrix}\psi_1\\ 0\end{bmatrix}\rightarrow\begin{cases}a=1\\ c=0\end{cases}$$

同理 $$\frac{\hbar}{2}\begin{bmatrix}a & b\\ c & d\end{bmatrix}\begin{bmatrix}0\\ \psi_2(\vec{r},t)\end{bmatrix}=-\frac{\hbar}{2}\begin{bmatrix}0\\ \psi_2(\vec{r},t)\end{bmatrix}\rightarrow\begin{bmatrix}b\psi_2\\ d\psi_2\end{bmatrix}\left(\quad\right)=-\begin{bmatrix}0\\ \psi_2\end{bmatrix}\rightarrow\begin{cases}b=0\\ d=-1\end{cases}$$

$$\hat{S}_z=\frac{\hbar}{2}\begin{bmatrix}1 & 0\\ 0 & -1\end{bmatrix}$$

因为 S_z 是 2 ×2 矩阵，所以在 S_z 为对角矩阵的表象内， $\chi_{1/2}$， $\chi_{-1/2}$ 都应是 2×1 的列矩阵。

$$\chi_{\frac{1}{2}}=\begin{bmatrix}a_1\\ a_2\end{bmatrix}\qquad \chi_{-\frac{1}{2}}=\begin{bmatrix}a_3\\ a_4\end{bmatrix}$$

$$\hat{S}_z = \frac{\hbar}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \qquad \chi_{\frac{1}{2}} = \begin{bmatrix} a_1 \\ a_2 \end{bmatrix} \qquad \chi_{-\frac{1}{2}} = \begin{bmatrix} a_3 \\ a_4 \end{bmatrix} \qquad \begin{cases} \hat{S}_z \chi_{\frac{1}{2}}(S_z) = \frac{\hbar}{2}\chi_{\frac{1}{2}}(S_z) \\ \hat{S}_z \chi_{-\frac{1}{2}}(S_z) = -\frac{\hbar}{2}\chi_{-\frac{1}{2}}(S_z) \end{cases}$$

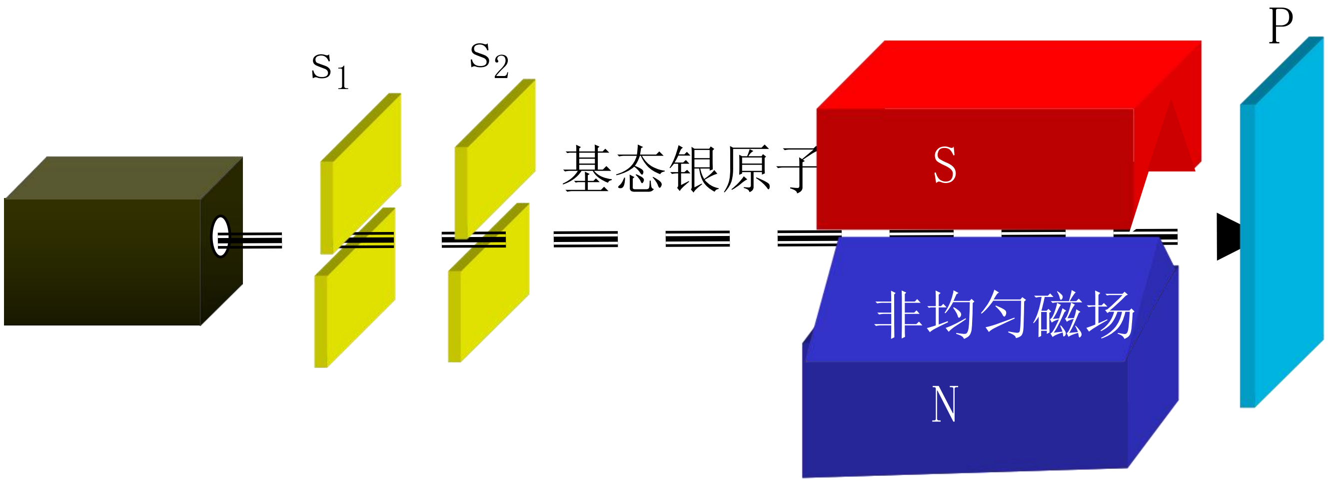
$$\frac{\hbar}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}\begin{bmatrix} a_1 \\ a_2 \end{bmatrix} = \frac{\hbar}{2}\begin{bmatrix} a_1 \\ a_2 \end{bmatrix} \to \begin{bmatrix} a_1 \\ -a_2 \end{bmatrix} = \begin{bmatrix} a_1 \\ a_2 \end{bmatrix} \to \begin{cases} a_1 = a_1 \\ a_2 = 0 \end{cases}$$

由归一化条件确定a_1 $\quad \begin{pmatrix} a_1^* & 0 \end{pmatrix}\begin{pmatrix} a_1 \\ 0 \end{pmatrix} = 1 \Rightarrow |a_1| = 1 \Rightarrow a_1 = 1 \quad \to \begin{cases} \chi_{\frac{1}{2}} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \\ \chi_{-\frac{1}{2}} = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \end{cases}$

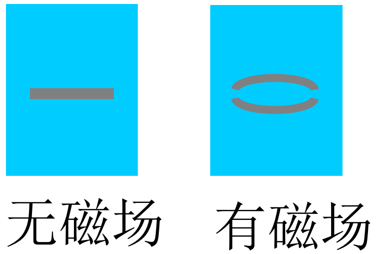
二者是属于不同本征值的本征函数，彼此应该正交

$$\chi_{-\frac{1}{2}}^{+}\chi_{\frac{1}{2}} = \begin{pmatrix} 0 & 1 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = 0$$

斯特恩—盖拉赫实验（1921）电子自旋自旋



实验结果：银原子束穿过非均匀磁场后分裂为两束。



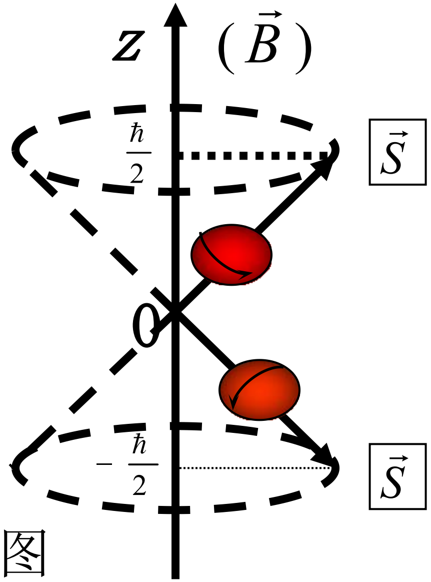
仿照电子的轨道运动，电子自旋角动量在 z 方向(外磁场方向)的分量取：

$$S_z = s\hbar,\quad -s\hbar = -\frac{\hbar}{2},\quad +\frac{\hbar}{2}$$

或：$$S_z = m_s\hbar$$

$$m_s = \pm s = \pm\frac{1}{2}$$

(m_s 称为自旋磁量子数)

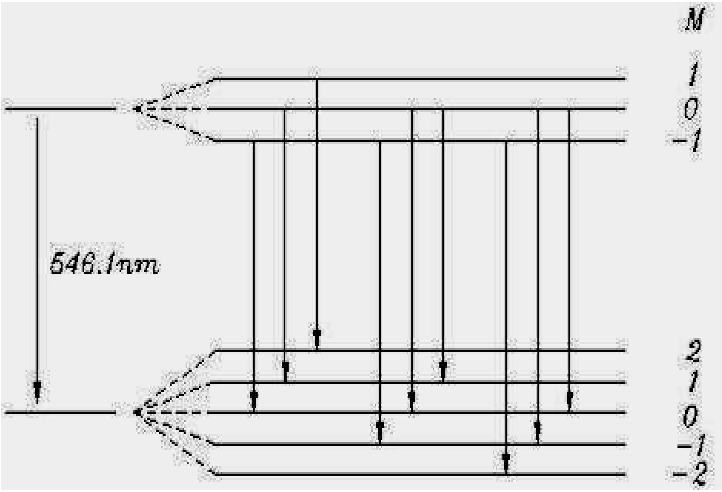


右图为电子在外磁场中的两种自旋运动状态的经典示意图

(自旋运动是相对论效应的必然结果，无经典运动对应)

5. 简单塞曼效应

塞曼效应：氢原子和类氢原子在外磁场中，其光谱线发生分裂的现象。现象在1896年被Zeeman首先 观察到



取外磁场方向沿 Z 向，则磁场引起的附加能为：

$$U=-(\hat{\vec{M}}_L+\hat{\vec{M}}_S)\bullet\vec{B}=\frac{q}{2\mu_{电子质量}c}(\hat{\vec{L}}+2\hat{\vec{S}})\bullet\vec{B}=\frac{q}{2\mu_{电子质量}c}(\hat{L}_z+2\hat{S}_z)B$$

$$\rightarrow\left(-\frac{\hbar^2}{2\mu}\nabla^2+U(r)+\frac{qB}{2\mu c}(\hat{L}_z+2\hat{S}_z)\right)\psi=E\psi$$

$$\begin{cases}\vec{S}_z=\pm\frac{1}{2}\hbar\\ L_z=\pm m\hbar\end{cases}\rightarrow\begin{cases}\left(-\frac{\hbar^2}{2\mu}\nabla^2+U(r)+\frac{qB}{2\mu c}(m\hbar+\hbar)\right)\psi_1=E\psi_1\\ \left(-\frac{\hbar^2}{2\mu}\nabla^2+U(r)+\frac{qB}{2\mu c}(m\hbar-\hbar)\right)\psi_2=E\psi_2\end{cases}$$

$$\begin{cases}\left(-\frac{\hbar^2}{2\mu}\nabla^2+U(r)\right)\psi_{nl}=E_{nl}\psi_{nl}\\ \left(-\frac{\hbar^2}{2\mu}\nabla^2+U(r)\right)\psi_{nl}=E_{nl}\psi_{nl}\end{cases}\rightarrow\begin{cases}\left(-\frac{\hbar^2}{2\mu}\nabla^2+U(r)+\frac{qB}{2\mu c}(m\hbar+\hbar)\right)\psi_1=E\psi_1\\ \left(-\frac{\hbar^2}{2\mu}\nabla^2+U(r)+\frac{qB}{2\mu c}(m\hbar-\hbar)\right)\psi_2=E\psi_2\end{cases}\rightarrow\begin{cases}E_{nlms}=E_{nl}+\frac{qB}{2\mu c}(m\hbar+\hbar)\\ E_{nlms}=E_{nl}+\frac{qB}{2\mu c}(m\hbar-\hbar)\end{cases}$$

$$E_{nlm}=\begin{cases} E_{nl}+\dfrac{e\hbar B}{2\mu c}(m+1) & S_z=\dfrac{\hbar}{2} \\ E_{nl}+\dfrac{e\hbar B}{2\mu c}(m-1) & S_z=-\dfrac{\hbar}{2} \end{cases}$$

（1）在外磁场下，能级与n, l, m有关。原来m不同能量相同的简并现象被外磁场消除了。

（2）外磁场存在时，能量与自旋状态有关。当原子处于S态时，$l=0,\ m=0$的原能级E_{nl}分裂为二。

$$E_{nlm}=E_{n00}=\begin{cases} E_{n0}+\dfrac{e\hbar B}{2\mu c} & (S_z=\dfrac{\hbar}{2}) \\ E_{n0}-\dfrac{e\hbar B}{2\mu c} & (S_z=-\dfrac{\hbar}{2}) \end{cases}$$

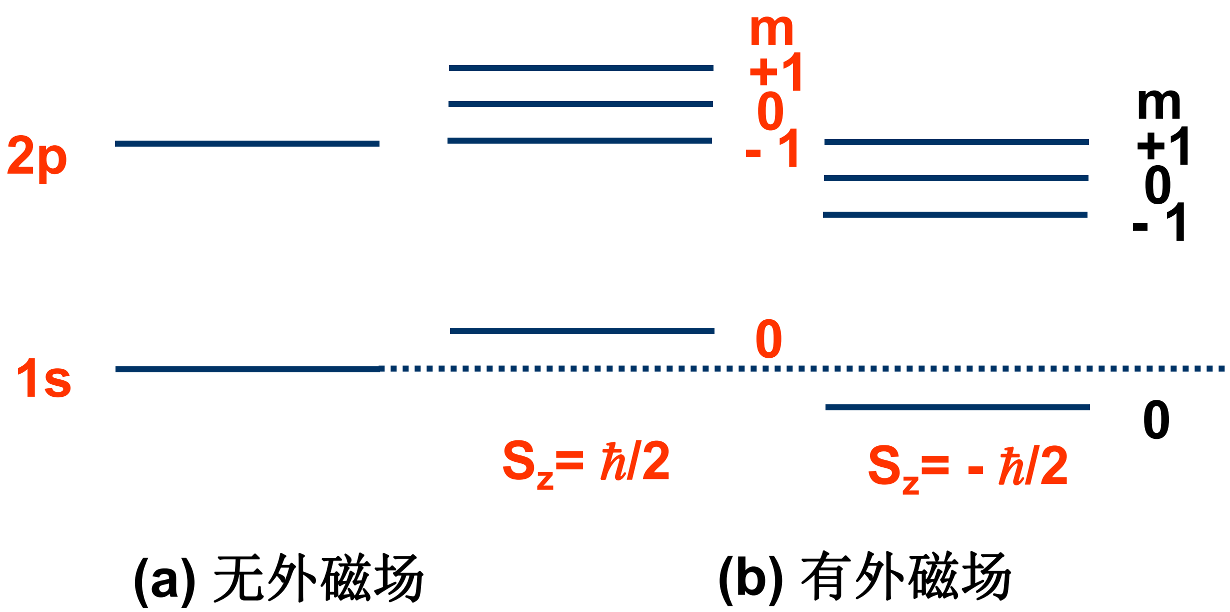
$$\omega = \frac{E_{nlm} - E_{n'l'm'}}{\hbar} = \frac{1}{\hbar}\left(E_{nl} + \frac{e\hbar B}{2\mu c}(m \pm 1) - E_{n'l'} + \frac{e\hbar B}{2\mu c}(m' \pm 1) \right)$$

$$= \frac{E_{nl} - E_{n'l'}}{\hbar} + \frac{e\hbar B}{2\mu c}(m \pm m') = \omega_0 + \frac{e\hbar B}{2\mu c}\Delta m$$

所以谱角频率可取三值:

$$\omega = \begin{cases} \omega_0 \\ \omega_0 + \dfrac{e\hbar B}{2\mu c} \\ \omega_0 - \dfrac{e\hbar B}{2\mu c} \end{cases}$$

（3）光谱线分裂



1902诺贝尔物理学奖得主

塞曼

塞曼效应的发现和研究

5.2. 多粒子体系与量子纠缠

1. 基本概念

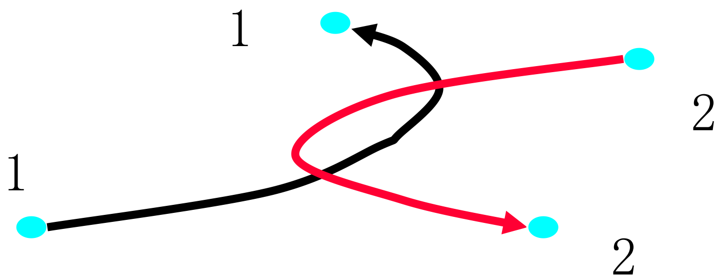
（1）全同粒子　　注意这里的自旋性质相同不代表自旋方向相同。

质量、电荷、自旋等固有性质完全相同的微观粒子。

（2）经典粒子的可区分性　而在量子力学中两个全同粒子是无法区分的。

经典力学中，固有性质完全相同的两个粒子，是可以区分的。因为二粒子在运动中，有各自确定的轨道，在任意时刻都有确定的位置和速度。

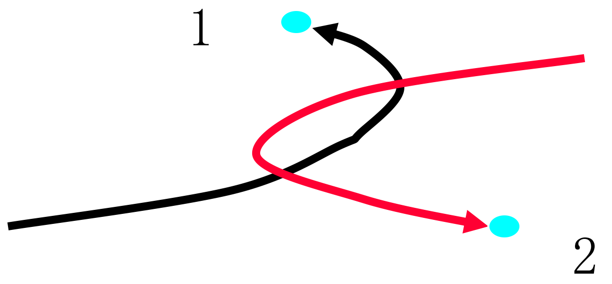
$$\left.\begin{cases}\text{位置}\\ \text{速度}\end{cases}\right. \Rightarrow \text{轨道}$$



可判断哪个是第一个粒子哪个是第二个粒子

$$\psi = \psi(q_1, q_2)$$

交换q_1, q_2位置 $\rightarrow \psi' = \psi(q_2, q_1)$



由于两个粒子不可区别：ψ和ψ'就是描写的同一状态，这就是量子力学不可区分原理

$$\begin{cases} \psi(q_2, q_1) = \lambda \psi(q_1, q_2) \\ \psi(q_1, q_2) = \lambda \psi(q_2, q_1) \end{cases} \rightarrow \lambda = \pm 1$$

$$\rightarrow \begin{cases} \psi(q_2, q_1) = \psi(q_1, q_2) \\ \psi(q_1, q_2) = -\psi(q_2, q_1) \end{cases}$$

2. Hamilton 算符的对称性

N个全同粒子：$\hat{H}(q_1,q_2,\cdots q_i\cdots q_j\cdots q_N,t)=\sum_{i=1}^{N}\left[-\frac{\hbar^2}{2\mu}\nabla_i^2+U(q_i,t)\right]+\sum_{i<j}^{N}U(q_i,q_j)$

其中$q_i=(\vec{r}_i,\vec{s}_i)$为第$i$个粒子的坐标和自旋。

注意电势能是相互作用能

由于第i和j粒子交换位置，q_i,和q_j位置交换:$\sum_{i<j}^{N}U(q_i,q_j)=\sum_{i<j}^{N}U(q_j,q_i)$

调换第i和第j粒子，体系$Hamilton$量不变:

$$\hat{H}(q_1,q_2,\cdots q_j\cdots q_i\cdots q_N,t)=\hat{H}(q_1,q_2,\cdots q_i\cdots q_j\cdots q_N,t)$$

表明，N 个全同粒子组成的体系的Hamilton 量具有交换对称性，交换任意两个粒子坐标（q_i, q_j）后不变。

（1）对称和反对称波函数

由于：$\hat{H}(q_1,q_2,\cdots q_j\cdots q_i\cdots q_N,t)=\hat{H}(q_1,q_2,\cdots q_i\cdots q_j\cdots q_N,t)$

$$\rightarrow\begin{cases} i\hbar\dfrac{\partial}{\partial t}\Phi(q_1,q_2,\cdots q_i\cdots q_j\cdots q_N,t)=\hat{H}(q_1,q_2,\cdots q_i\cdots q_j\cdots q_N,t)\Phi(q_1,q_2,\cdots q_i\cdots q_j\cdots q_N,t) \\ i\hbar\dfrac{\partial}{\partial t}\Phi(q_1,q_2,\cdots q_j\cdots q_i\cdots q_N,t)=\hat{H}(q_1,q_2,\cdots q_j\cdots q_i\cdots q_N,t)\Phi(q_1,q_2,\cdots q_j\cdots q_i\cdots q_N,t) \end{cases}$$

$\begin{cases}\Phi(q_1,q_2,\cdots q_i\cdots q_j\cdots q_N,t) \\ \Phi(q_1,q_2,\cdots q_j\cdots q_i\cdots q_N,t)\end{cases}$ $\rightarrow$描写同一状态, 因此，二者相差一常数因子

$$\begin{cases}\Phi(q_1,q_2,\cdots q_j\cdots q_i\cdots q_N,t)=\lambda\Phi(q_1,q_2,\cdots q_i\cdots q_j\cdots q_N,t) \\ \Phi(q_1,q_2,\cdots q_i\cdots q_j\cdots q_N,t)=\lambda\Phi(q_1,q_2,\cdots q_j\cdots q_i\cdots q_N,t)\end{cases}\rightarrow\lambda^2=1$$

所以$\lambda^2=1 \qquad \Rightarrow\lambda=\pm1$

$$\begin{cases} \lambda=1\text{二粒子互换后波函数不变，}\Phi(q_1,q_2,\cdots q_i\cdots q_j\cdots q_N,t)=\Phi(q_1,q_2,\cdots q_j\cdots q_i\cdots q_N,t):\text{波函数对称} \\ \lambda=-1\text{二粒子互换后波函数变号，}\Phi(q_1,q_2,\cdots q_i\cdots q_j\cdots q_N,t)=-\Phi(q_1,q_2,\cdots q_j\cdots q_i\cdots q_N,t)\text{： 波函数反对称} \end{cases}$$

$$\to \begin{cases} \hat{P}_{ij}\Phi(i,j)=\Phi(j,i)=\lambda\Phi(i,j) \\ \hat{P}_{ij}^{2}\Phi(i,j)=\hat{P}_{ij}\hat{P}_{ij}\Phi(i,j)=\lambda\hat{P}_{ij}\Phi(i,j)=\lambda^{2}\Phi(i,j) \end{cases}$$

$$\to\text{所以}\qquad \lambda=\pm1,\begin{cases} \text{对称波函数是}\hat{P}_{ij}\text{本征值},\ \lambda=+1\text{的本征态；} \\ \text{反对称波函数是}\hat{P}_{ij}\text{本征值}\lambda=-1\text{的本征态。} \end{cases}$$

3. Fermi 子和 Bose 子

实验表明：对于每一种粒子，它们的多粒子波函数的交换对称性是完全确定的，而且该对称性与粒子的自旋有确定的联系。

（1）Bose 子

凡自旋为 $\hbar$ 整数倍（s = 0，1，2，……）的粒子，其多粒子波函数对于交换2个粒子总是对称的，遵从Bose统计，故称为Bose子

如：γ 光子 （s =1）；π 介子 （s = 0）。

（2）Fermi 子

凡自旋为 $\hbar$ 半奇数倍（s =1/2，3/2，……）的粒子，其多粒子波函数对于交换2个粒子总是反对称的，遵从Fermi统计，故称为Fermi子。

例如：电子、质子、中子（ s =1/2）等粒子。

4. 两粒子的状态

- 两个完全相同粒子构成的系统

2个全同粒子Hamilton 量(假如它们之间无相互作用)

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla_1^2 - \frac{\hbar^2}{2\mu}\nabla_2^2 + U(q_1) + U(q_2) = \hat{H}_0(q_1) + \hat{H}_0(q_2)$$

II 单粒子波函数

$\hat{H}_0$对全同粒子是一样的，设其不显含时间，则$\begin{cases} \hat{H}_0(q_1)\psi_1(q_1) = E_1\psi_1(q_1) \\ \hat{H}_0(q_2)\psi_2(q_2) = E_2\psi_2(q_2) \end{cases}$

$\psi_i(q_n)(n=1,2.)$ 称为单粒子波函数。

III　交换简并粒子1是A态，粒子2是B态，则体系能量和波函数为：

$$\begin{cases}\hat{H}_0(q_1)\psi_i(q_1)=E_1\psi_1(q_{A1})\\ \hat{H}_0(q_2)\psi_j(q_2)=E_2\psi_2(q_{B2})\end{cases}\rightarrow E=E_1+E_2\rightarrow\begin{cases}\hat{H}\Phi_1\left(q_{A1},q_{B2}\right)=E\Phi_1\left(q_{A1},q_{B2}\right)\\ \hat{H}\Phi_2\left(q_{B1},q_{A2}\right)=E\Phi_2\left(q_{B1},q_{A2}\right)\end{cases}$$

证明：$\left[\hat{H}_0(q_1)+\hat{H}_0(q_2)\right]\Phi_1\left(q_1,q_2\right)=[\hat{H}_0(q_1)+\hat{H}_0(q_2)]\psi_1(q_{A1})\psi_2(q_{B2})$

$$=\left[\hat{H}_0(q_{A1})\psi_1(q_{A1})\right]\psi_2(q_{B2})+\psi_1(q_{A1})\left[\hat{H}_0(q_{B2})\psi_2(q_{B2})\right]$$

此段说明能量是简并的。

$$=E_1\psi_1(q_{A1})\psi_2(q_{B2})+E_2\psi_1(q_{A1})\psi_2(q_{B2})=(E_1+E_2)\psi_1(q_{A1})\psi_2(q_{B2})=E\Phi\left(q_{A1},q_{B2}\right)$$

$$\rightarrow\begin{cases}\hat{H}_{AB}\Phi_1\left(q_{A1},q_{B2}\right)=E\Phi_1\left(q_{A1},q_{B2}\right)\\ \hat{H}_{AB}\Phi_2\left(q_{B1},q_{A2}\right)=E\Phi_2\left(q_{B1},q_{A2}\right)\end{cases}\rightarrow\begin{cases}\Phi_1\left(q_{A1},q_{B2}\right)=\psi_1\left(q_{A1}\right)\psi_2\left(q_{B2}\right)\\ \Phi_2\left(q_{B1},q_{A2}\right)=\psi_1\left(q_{B1}\right)\psi_2\left(q_{A2}\right)\end{cases}$$

状态$\Phi_1\left(q_{1A},q_{2B}\right)$和$\Phi_2\left(q_{1B},q_{2A}\right)$能量是简并的，由于这两种状态可通过$q_1\Leftrightarrow q_2$互换得到，故称该简并为交换简并。

IV　满足对称条件波函数的构成

(或者反对称性)

全同粒子体系要满足对称性条件，而$\Phi_1(q_{1A}, q_{2B})$和$\Phi_2(q_{1B}, q_{2A})$仅当$A=B$二态相同时，才是一个对称波函数；

(主要是指自旋方向相同)

当$A\neq B$二态不同时，既不是对称波函数，也不是反对称波函数。所以$\Phi_1(q_1, q_2)$和Φ_2 (q_2, q_1)不能用来描写全同粒子体系。

构造具有对称性的波函数

$$\begin{cases} \Phi_+(q_1,q_2)=C\left[\Phi_1(q_{A1},q_{B2})+\Phi_2(q_{B1},q_{A2})\right] \\ \Phi_-(q_1,q_2)=C\left[\Phi_1(q_{A1},q_{B2})-\Phi_2(q_{B1},q_{A2})\right] \end{cases} \rightarrow C\text{是系数}$$

显然 Φ_+ (q_1, q_2) 和 Φ_- (q_1, q_2) 都是H的本征函数，本征值皆为：

$$\rightarrow E=E_i+E_j$$

V 归一化

若单粒子波函数是正交归一化的，则$\Phi_1(q_1, q_2)$和$\Phi_2(q_2, q_1)$也是正交归一化的

证：$\iint \Phi^*{}_1(q_{A1}, q_{B2})\Phi_1(q_{A1}, q_{B2})dq_1dq_2 = \iint \psi_i^*(q_{A1}))\psi_j^*(q_{B2})\psi_i(q_{A1})\psi_j(q_{B2})dq_1dq_2$

$$= \int \psi_i^*(q_{A1})\psi_i(q_{A1})dq_1 \int \psi_j^*(q_{B2})\psi_j(q_{B2})dq_2 = 1$$

同理 $\rightarrow \iint \Phi_2{}^*(q_{B1}, q_{A2})\Phi_2(q_{B1}, q_{A2})dq_1dq_2 = 1$

但是 $\rightarrow \iint \Phi_2{}^*(q_{A1}, q_{B2})\Phi_1(q_{B1}, q_{A2})dq_{A1}dq_{B2} = \iint \psi_i^*(q_{A1})\psi_j^*(q_{B2})\psi_i(q_{B1})\psi_j(q_{A2})dq_1dq_2$

$$= \int \psi_j^*(q_{A1})\psi_i(q_{B2})dq_1 \int \psi_i^*(q_{B1})\psi_j(q_{A2})dq_2 = 0$$

同理 $\rightarrow \iint \Phi_1{}^*(q_{A1}, q_{B2})\Phi_2(q_{B1}, q_{A2})dq_1dq_2 = 0$

C系数的计算

$$\begin{cases}\hat{H}_{AB}\Phi_1(q_{A1},q_{B2})=E\Phi_1(q_{A1},q_{B2})\\ \hat{H}_{AB}\Phi_2(q_{A2},q_{B1})=E\Phi_2(q_{A2},q_{B1})\end{cases}\rightarrow\begin{cases}\Phi_1(q_{A1},q_{B2})=\psi_i(q_{A1})\psi_j(q_{B2})\\ \Phi_2(q_{B1},q_{A2})=\psi_i(q_{B1})\psi_j(q_{A2})\end{cases}$$

$$\rightarrow\begin{cases}\iint\Phi^*_1(q_{A1},q_{B2})\Phi_1(q_{A1},q_{B2})dq_1dq_2=1 & \iint\Phi_2^*(q_{B1},q_{A2})\Phi_2(q_{B1},q_{A2})dq_1dq_2=1\\ \iint\Phi_2^*(q_{A1},q_{B2})\Phi_1(q_{B1},q_{A2})dq_1dq_2=0 & \iint\Phi_1^*(q_{B1},q_{A2})\Phi_2(q_{A1},q_{B2})dq_1dq_2=0\end{cases}$$

构建函数: $\begin{cases}\Phi_+(q_1,q_2)=C\left[\Phi_1(q_{A1},q_{B2})+\Phi_2(q_{A2},q_{B1})\right]\\ \Phi_-(q_1,q_2)=C\left[\Phi_1(q_{A1},q_{B2})-\Phi_2(q_{A2},q_{B1})\right]\end{cases}\rightarrow C$是系数

$$\int\Phi_+^*(q_1,q_2)\Phi_+(q_1,q_2)dq_1dq_2=\int C^2\left[\Phi_1^*(q_{A1},q_{B2})+\Phi_2^*(q_{A2},q_{B1})\right]\left[\Phi_1(q_{A1},q_{B2})+\Phi_2(q_{A2},q_{B1})\right]dq_1dq_2$$

$$\int\Phi_+^*(q_1,q_2)\Phi_+(q_1,q_2)dq_1dq_2$$

$$=\int C^2\left[\Phi_1^*(q_{A1},q_{B2})\Phi_1(q_{A1},q_{B2})+\Phi_2^*(q_{A2},q_{B1})\Phi_1(q_{A1},q_{B2})+\Phi_1^*(q_{A1},q_{B2})\Phi_2(q_{A2},q_{B1})+\Phi_2^*(q_{A2},q_{B1})\Phi_2(q_{A2},q_{B1})\right]dq_1dq_2$$

$$\text{利用}\rightarrow\begin{cases}\iint\Phi^*{}_1\left(q_{A1},q_{B2}\right)\Phi_1\left(q_{A1},q_{B2}\right)dq_1dq_2=1\\ \iint\Phi_2{}^*\left(q_{A2},q_{B1}\right)\Phi_2\left(q_{A2},q_{B1}\right)dq_1dq_2=1\\ \iint\Phi_2{}^*\left(q_{A2},q_{B1}\right)\Phi_1\left(q_{A1},q_{B2}\right)dq_1dq_2=0\\ \iint\Phi_1{}^*\left(q_{A1},q_{B2}\right)\Phi_2\left(q_{A2},q_{B1}\right)dq_1dq_2=0\end{cases}$$

$$\int\Phi_+^*(q_1,q_2)\Phi_+(q_1,q_2)dq_1dq_2=\int C^2\begin{bmatrix}\Phi_1^*\left(q_{A1},q_{B2}\right)\Phi_1\left(q_{A1},q_{B2}\right)+\Phi_2^*\left(q_{A2},q_{B1}\right)\Phi_1\left(q_{A1},q_{B2}\right)\\ +\Phi_1^*\left(q_{A1},q_{B2}\right)\Phi_2\left(q_{A2},q_{B1}\right)+\Phi_2^*\left(q_{A2},q_{B1}\right)\Phi_2\left(q_{A2},q_{B1}\right)\end{bmatrix}dq_1dq_2$$

$$\int\Phi_+^*(q_1,q_2)\Phi_+(q_1,q_2)dq_1dq_2=C^2\left[1+0+0+1\right]=1\qquad C=\frac{1}{\sqrt{2}}$$

$$\text{利用}C=\frac{1}{\sqrt{2}}\rightarrow\begin{cases}\Phi_+(q_1,q_2)=\dfrac{1}{\sqrt{2}}\left[\Phi_1\left(q_{A1},q_{B2}\right)+\Phi_2\left(q_{A2},q_{B1}\right)\right]\\ \Phi_-(q_1,q_2)=\dfrac{1}{\sqrt{2}}\left[\Phi_1\left(q_{A1},q_{B2}\right)-\Phi_2\left(q_{A2},q_{B1}\right)\right]\end{cases}$$

●2个全同粒子Hamilton 量(它们之间有相互作用)

$$\hat{H}=-\frac{\hbar^2}{2\mu}\nabla_1^2-\frac{\hbar^2}{2\mu}\nabla_2^2+U(q_1)+U(q_2)+\Delta U_{\text{相互作用能量}}\neq\hat{H}_0(q_1)+\hat{H}_0(q_2)$$

$$\rightarrow\begin{cases}\Phi_1(q_{A1},q_{B2})\neq\psi_i(q_{A1})\varphi_j(q_{B2})\\ \Phi_2(q_{A2},q_{B1})\neq\psi_i(q_{A2})\varphi_j(q_{B1})\end{cases}$$

但是 $\rightarrow\begin{cases}\hat{H}(q_1,q_2)\Phi(q_{A1},q_{B2})=E\Phi(q_{A1},q_{B2})\\ \hat{H}(q_1,q_2)\Phi(q_{B2},q_{A1})=E\Phi(q_{A2},q_{B1})\end{cases}$

仍满足能量的简并性

$$\rightarrow\begin{cases}\Phi_+(q_1,q_2)=\frac{1}{\sqrt{2}}[\Phi_1(q_{A1},q_{B2})\pm\Phi_2(q_{A2},q_{B1})]\\ \Phi_-(q_1,q_2)=\frac{1}{\sqrt{2}}[\Phi_1(q_{A1},q_{B2})\pm\Phi_2(q_{A2},q_{B1})]\end{cases}$$

因H 的对称性式2成立

泡利不相容原理

如果有N个粒子

$$\hat{H}=\hat{H}_0(q_1)+\hat{H}_0(q_2)+\ldots+\hat{H}_0(q_N)=\sum_{i=1}^{N}\hat{H}_0(q_i)$$

$$\begin{cases}\hat{H}_0(q_1)\psi_i(q_1)=E_1\psi_1(q_{A1})\\ \hat{H}_0(q_2)\psi_j(q_2)=E_2\psi_2(q_{B2})\\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\\ \hat{H}_0(q_N)\psi_k(q_N)=E_N\psi_k(q_{kN})\end{cases}$$

$$\to\hat{H}\Phi=E\Phi\to\begin{cases}E=E_1+E_2+\ldots+E_N\\ \Phi=\psi_1(q_{1A})\psi_2(q_{2B})\ldots\psi_N(q_{Nk})\end{cases}$$

$$\left[\hat{H}_0(q_1)+\hat{H}_0(q_2)+\ldots+\hat{H}_0(q_N)\right]\left[\psi_1(q_{1A})\psi_2(q_{2B})\ldots\psi_N(q_{Nk})\right]$$

$$=\left[\hat{H}_0(q_1)\right]\left[\psi_1(q_{1A})\psi_2(q_{2B})\ldots\psi_N(q_{Nk})\right]+\left[\hat{H}_0(q_2)\right]\left[\psi_1(q_{1A})\psi_2(q_{2B})\ldots\psi_N(q_{Nk})\right]+\ldots\ldots+\left[\hat{H}_0(q_N)\right]\left[\psi_1(q_{1A})\psi_2(q_{2B})\ldots\psi_N(q_{Nk})\right]$$

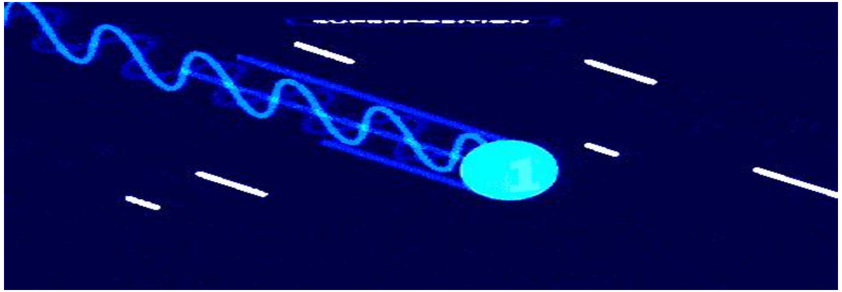
$$=E_1\left[\psi_1(q_{1A})\psi_2(q_{2B})\ldots\psi_N(q_{Nk})\right]+E_2\left[\psi_1(q_{1A})\psi_2(q_{2B})\ldots\psi_N(q_{Nk})\right]+\ldots\ldots+E_N\left[\psi_1(q_{1A})\psi_2(q_{2B})\ldots\psi_N(q_{Nk})\right]=(E_1+E_2+\ldots E_N)\Phi$$

对于费米子，构建对称函数：$\Phi_A = \frac{1}{\sqrt{N\downarrow}} \begin{vmatrix} \psi_1(q_{1A}) & \psi_2(q_{2A}) & \cdots & \psi_N(q_{NA}) \\ \psi_1(q_{1B}) & \psi_2(q_{2B}) & \cdots & \psi_N(q_{NB}) \\ \cdots & \cdots & \cdots & \cdots \\ \psi_1(q_{1k}) & \psi_2(q_{2k}) & \cdots & \psi_N(q_{Nk}) \end{vmatrix}$

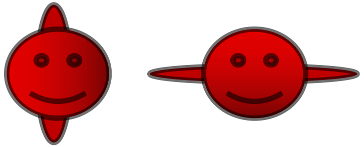
对于费米子，如果两个粒子相同：$\Phi_A = \frac{1}{\sqrt{N\downarrow}} \begin{vmatrix} \psi_1(q_{1A}) & \psi_2(q_{2A}) & \cdots & \psi_N(q_{NA}) \\ \psi_1(q_{1A}) & \psi_2(q_{2A}) & \cdots & \psi_N(q_{NA}) \\ \cdots & \cdots & \cdots & \cdots \\ \psi_1(q_{1k}) & \psi_2(q_{2k}) & \cdots & \psi_N(q_{Nk}) \end{vmatrix} = 0$

则不存在这样的对称函数，违反全同粒子状态存在条件

5.3　量子纠缠实验验证



光子



总 结

量子：

虽然哥永远传说，要相信哥！