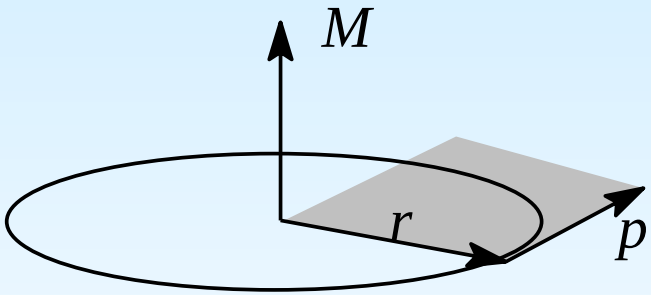
第三章 角动量和自旋

Angular Momentum and Electron Spin

§3.1 角动量算符 The angular mementum operators

经典力学：质点的角动量M定义为向径r与线性动量p的矢积



$$\vec{M} = \vec{r} \times \vec{p} = \begin{vmatrix} \vec{i} & \vec{j} & \vec{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$

$$= (yp_z - zp_y)\vec{i} + (zp_x - xp_z)\vec{j} + (xp_y - yp_x)\vec{k}$$

$$= M_x\vec{i} + M_y\vec{j} + M_z\vec{k}$$

角动量M的三个分量M_x M_y M_z分别为

$$M_x = yp_z - zp_y$$

$$M_y = zp_x - xp_z$$

$$M_z = xp_y - yp_x$$

$$M^2 = M_x^2 + M_y^2 + M_z^2$$

量子力学

$$\hat{M}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$

$$\hat{M}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$

$$\hat{M}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

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

球坐标系

$$\begin{cases} x = r\sin\theta\cos\phi \\ y = r\sin\theta\sin\phi \\ z = r\cos\theta \end{cases} \Rightarrow \begin{cases} \cos\theta = z\Big/\sqrt{x^2+y^2+z^2} \\ \tan\phi = y/x \\ r^2 = x^2+y^2+z^2 \end{cases}$$

$$\left.\begin{aligned} \frac{\partial r}{\partial z} &= \cos\theta & \frac{\partial r}{\partial y} &= \sin\theta\sin\phi \\ \frac{\partial \theta}{\partial z} &= -\frac{\sin\theta}{r} & \frac{\partial \theta}{\partial y} &= \frac{\cos\theta\sin\phi}{r} \\ \frac{\partial \phi}{\partial z} &= 0 & \frac{\partial \phi}{\partial y} &= \frac{\cos\phi}{r\sin\theta} \end{aligned}\right\}$$

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

$$= -i\hbar\left[r\sin\theta\sin\phi\left(\frac{\partial r}{\partial z}\frac{\partial}{\partial r} + \frac{\partial\theta}{\partial z}\frac{\partial}{\partial\theta} + \frac{\partial\phi}{\partial z}\frac{\partial}{\partial\phi}\right) - r\cos\theta\left(\frac{\partial r}{\partial y}\frac{\partial}{\partial r} + \frac{\partial\theta}{\partial y}\frac{\partial}{\partial\theta} + \frac{\partial\phi}{\partial y}\frac{\partial}{\partial\phi}\right)\right]$$

$$= -i\hbar\left[r\sin\theta\sin\phi\left(\cos\theta\frac{\partial}{\partial r} - \frac{\sin\theta}{r}\frac{\partial}{\partial\theta}\right) - r\cos\theta\left(\sin\theta\sin\phi\frac{\partial}{\partial r} + \frac{\cos\theta\sin\phi}{r}\frac{\partial}{\partial\theta} + \frac{\cos\phi}{r\sin\theta}\frac{\partial}{\partial\phi}\right)\right]$$

$$= i\hbar\left(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right)$$

$$\hat{M}_x = i\hbar\left(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right)$$

$$\hat{M}_y = -i\hbar\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)$$

$$\hat{M}_z = -i\hbar\frac{\partial}{\partial\phi}$$

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

角动量算符对易规则

$$\left[\hat{M}_x,\hat{M}_y\right]=\left[(y\hat{p}_z-z\hat{p}_y),(z\hat{p}_x-x\hat{p}_z)\right]$$

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

$$=y\hat{p}_z(z\hat{p}_x)-yz\hat{p}_x\hat{p}_z-0-0+zx\hat{p}_y\hat{p}_z-x\hat{p}_z(z\hat{p}_y)$$

$$=-i\hbar y\hat{p}_x+i\hbar x\hat{p}_y=i\hbar\hat{M}_z$$

$$\boxed{\left[\hat{M}_x,\hat{M}_y\right]=i\hbar\hat{M}_z\quad\left[\hat{M}_y,\hat{M}_z\right]=i\hbar\hat{M}_x\quad\left[\hat{M}_z,\hat{M}_x\right]=i\hbar\hat{M}_y}$$

$$\left[\hat{M}^2,\hat{M}_x\right]=\left[\hat{M}_x^2,\hat{M}_x\right]+\left[\hat{M}_y^2,\hat{M}_x\right]+\left[\hat{M}_z^2,\hat{M}_x\right]$$

$$=\left[\hat{M}_y,\hat{M}_x\right]\hat{M}_y+\hat{M}_y\left[\hat{M}_y,\hat{M}_x\right]+\left[\hat{M}_z,\hat{M}_x\right]\hat{M}_z+\hat{M}_z\left[\hat{M}_z,\hat{M}_x\right]$$

$$=-i\hbar\hat{M}_z\hat{M}_y-i\hbar\hat{M}_y\hat{M}_z+i\hbar\hat{M}_y\hat{M}_z+i\hbar\hat{M}_z\hat{M}_y=0$$

$$\boxed{\left[\hat{M}^2,\hat{M}_x\right]=\left[\hat{M}^2,\hat{M}_y\right]=\left[\hat{M}^2,\hat{M}_z\right]=0}$$

Hamilton算符与角动量算符的对易规则

$$\hat{H}=\hat{T}+\hat{V}=-\frac{\hbar^2}{2m}\nabla^2+V$$

对单质点体系，V与θ,ϕ无关

$$\nabla^2=\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}$$

$$=\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}-\frac{1}{r^2\hbar^2}\hat{M}^2$$

$$\left[\nabla^2,\hat{M}^2\right]=0 \Longrightarrow \boxed{\left[\hat{H},\hat{M}^2\right]=0}$$

$$\left[\hat{M}^2,\hat{M}_x\right]=\left[\hat{M}^2,\hat{M}_y\right]=\left[\hat{M}^2,\hat{M}_z\right]=0$$

$$\boxed{\left[\hat{H},\hat{M}_x\right]=\left[\hat{H},\hat{M}_y\right]=\left[\hat{H},\hat{M}_z\right]=0}$$

$$\left[\hat{H},\hat{M}^2\right]=0 \quad \left[\hat{H},\hat{M}_z\right]=0 \quad \left[\hat{M}^2,\hat{M}_z\right]$$

两两相互对易，可以同时具有确定值

类氢原子体系：

$$\hat{H}\psi_{nlm}=E_n\psi_{nlm}$$

$$\hat{M}^2\psi_{nlm}=l(l+1)\hbar^2\psi_{nlm}$$

$$\hat{M}_z\psi_{nlm}=m\hbar\psi_{nlm}$$

$$E=-\frac{\mu e^4}{8\varepsilon_0^2h^2}\cdot\frac{Z^2}{n^2}$$

$$M^2=l(l+1)\hbar^2 \qquad |M|=\sqrt{l(l+1)}\hbar$$

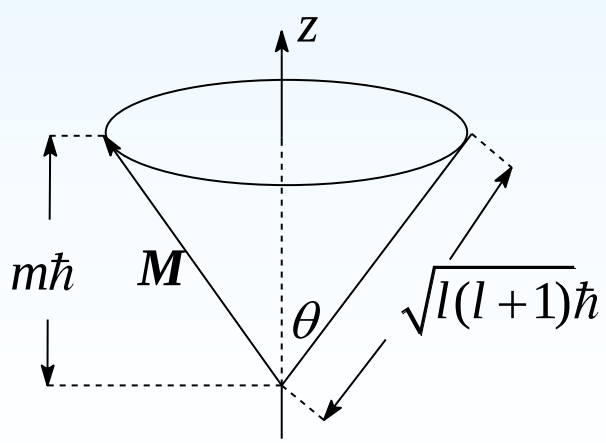
$$M_z=m\hbar$$

M的大小可以确定，但方向不能确定

$$\left[\phi,\hat{M}_z\right]=\left[\phi,-i\hbar\frac{\partial}{\partial\phi}\right]=-i\hbar\phi\frac{\partial}{\partial\phi}+i\hbar+i\hbar\phi\frac{\partial}{\partial\phi}=i\hbar$$

$$\overline{(\Delta\phi)^2}\,\overline{(\Delta M_z)^2}\geq-\frac{1}{4}\left[\int\psi^*\left[\phi,\hat{M}_z\right]\psi d\tau\right]^2=\frac{1}{4}\hbar^2$$ *Heiseberg* 不确定关系

$$\Delta\phi\Delta M_z\geq\frac{1}{2}\hbar$$ M_z具有确定值，ϕ完全不能确定



$$\cos\theta=\frac{m}{\sqrt{l(l+1)}}$$

§ 3.2 阶梯算符 The ladder operators

$$\hat{M}_+ \equiv \hat{M}_x + i\hat{M}_y$$ 递升算符 *step-up or raising operator*

$$\hat{M}_- \equiv \hat{M}_x - i\hat{M}_y$$ 递减算符 *step-down or lowering operator*

$$\boxed{\begin{aligned}\left[\hat{M}_+,\hat{M}^2\right] &= \left[\hat{M}_x,\hat{M}^2\right] + i\left[\hat{M}_y,\hat{M}^2\right] = 0\\ \left[\hat{M}_-,\hat{M}^2\right] &= \left[\hat{M}_x,\hat{M}^2\right] - i\left[\hat{M}_y,\hat{M}^2\right] = 0\end{aligned}}$$

$$\left[\hat{M}_+,\hat{M}_z\right] = \left[\hat{M}_x,\hat{M}_z\right] + i\left[\hat{M}_y,\hat{M}_z\right] = -i\hbar\hat{M}_y - \hbar\hat{M}_x = -\hbar\hat{M}_+$$

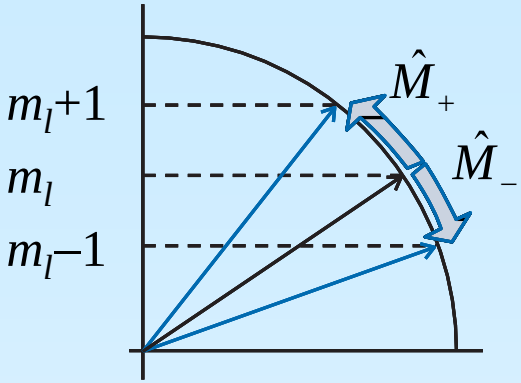
$$\hat{M}_+\hat{M}_z = \hat{M}_z\hat{M}_+ - \hbar\hat{M}_+ = (\hat{M}_z - \hbar)\hat{M}_+$$

$$\hat{M}_-\hat{M}_z = \hat{M}_z\hat{M}_- + \hbar\hat{M}_- = (\hat{M}_z + \hbar)\hat{M}_-$$

$$\begin{aligned}\hat{M}_+\hat{M}_- &= \left(\hat{M}_x + i\hat{M}_y\right)\left(\hat{M}_x - i\hat{M}_y\right) = \hat{M}_x^2 + \hat{M}_y^2 + i\left(\hat{M}_y\hat{M}_x - \hat{M}_x\hat{M}_y\right)\\ &= \hat{M}^2 - \hat{M}_z^2 + \hbar\hat{M}_z\end{aligned}$$

$$\hat{M}_-\hat{M}_+ = \hat{M}^2 - \hat{M}_z^2 - \hbar\hat{M}_z$$

阶梯算符法求角动量的本征值



$\hat{M}^2, \hat{M}_z$ 共同的本征函数Y，设 $\begin{cases} \hat{M}^2 Y = cY \\ \hat{M}_z Y = bY \end{cases}$

$$\left.\begin{aligned} \hat{M}_+\hat{M}_z Y &= \hat{M}_+ bY = b\hat{M}_+ Y \\ \hat{M}_+\hat{M}_z Y &= \hat{M}_z\hat{M}_+ Y - \hbar\hat{M}_+ Y \end{aligned}\right\} \Rightarrow \hat{M}_z(\hat{M}_+ Y) = (b+\hbar)\hat{M}_+ Y$$

$$Y' = \hat{M}_+ Y$$

$$\hat{M}_z Y' = (b+\hbar)Y'$$

$\boldsymbol{M}_+$作用在Y上，得到新函数Y'，Y'也是$\boldsymbol{M}_z$的本征函数，但本征值增加了$\hbar$，这就是递升算符名称的来源

$$\hat{M}_+\hat{M}_z(\hat{M}_+ Y) = (b+\hbar)\hat{M}_+^2 Y$$

$$(\hat{M}_z\hat{M}_+ - \hbar\hat{M}_+)(\hat{M}_+ Y) = \hat{M}_z\hat{M}_+^2 Y - \hbar\hat{M}_+^2 Y = (b+\hbar)\hat{M}_+^2 Y$$

$$\hat{M}_z\hat{M}_+^2 Y = (b+2\hbar)\hat{M}_+^2 Y$$

$$\hat{M}_z\hat{M}_+^k Y = (b+k\hbar)\hat{M}_+^k Y$$

$$\hat{M}_z\hat{M}_-^k Y = (b-k\hbar)\hat{M}_-^k Y \qquad k=0, 1, 2\ldots$$

$\hat{M}_\pm^k Y$ 是 $\hat{M}_z$ 的本征函数

$$\left[\hat{M}^2, \hat{M}_\pm\right] = 0$$

$$\left[\hat{M}^2, \hat{M}_\pm^2\right] = \left[\hat{M}^2, \hat{M}_\pm\right]\hat{M}_\pm + \hat{M}_\pm\left[\hat{M}^2, \hat{M}_\pm\right] = 0$$

$$\left[\hat{M}^2, \hat{M}_\pm^k\right] = 0$$

$\hat{M}_\pm^k$ 与 $\hat{M}^2$ 对易

$$\hat{M}^2(\hat{M}_\pm^k Y) = \hat{M}^2 Y_k$$

$$\hat{M}^2(\hat{M}_\pm^k Y) = \hat{M}_\pm^k \hat{M}^2 Y = c\hat{M}_\pm^k Y = cY_k$$

$$\Longrightarrow \hat{M}^2 Y_k = cY_k$$

$$\hat{M}_z Y = bY \quad \hat{M}_z Y_k = b_k Y_k \qquad Y_k = \hat{M}_\pm^k Y \quad b_k = b \pm k\hbar$$

$$\hat{M}_z^2 Y_k = b_k^2 Y_k$$

$$\left(\hat{M}^2 - \hat{M}_z^2\right)Y_k = \left(c - b_k^2\right)Y_k$$

$$\left(\hat{M}_x^2 + \hat{M}_y^2\right)Y_k = \left(c - b_k^2\right)Y_k$$

$$c - b_k^2 \geq 0 \qquad \sqrt{c} \geq b_k \geq -\sqrt{c}$$

设$b_{\max}$与$b_{\min}$分别为b_k的极大极小值，对应的函数为$Y_{\max}$和$Y_{\min}$

$$\hat{M}_z Y_{\max} = b_{\max} Y_{\max}$$

$$\hat{M}_z Y_{\min} = b_{\min} Y_{\min}$$

$$\hat{M}_+\hat{M}_z Y_{\max} = b_{\max}\hat{M}_+ Y_{\max}$$

$$\hat{M}_z(\hat{M}_+ Y_{\max}) = (b_{\max} + \hbar)\hat{M}_+ Y_{\max} \Rightarrow \hat{M}_+ Y_{\max} = 0$$

$$\hat{M}_-\hat{M}_+ Y_{\max} = (\hat{M}^2 - \hat{M}_z^2 - \hbar\hat{M}_z)Y_{\max} = c - b_{\max}^2 - \hbar b_{\max} = 0$$

同理 $c - b_{\min}^2 + \hbar b_{\min} = 0$

$$(b_{\max} + b_{\min})(b_{\max} - b_{\min} + \hbar) = 0$$

$$\Downarrow$$

$$\left.\begin{array}{l} b_{\max} = -b_{\min} \\ b_{\max} - b_{\min} = n\hbar \end{array}\right\} \Longrightarrow \quad b_{\max} = \frac{1}{2}n\hbar$$

令 $j = \frac{1}{2}n$ $\qquad b = m_j\hbar \qquad (m_j = -j, -j+1, \ldots, j-1, j)$

$c = j(j+1)\hbar^2 \qquad (j = 0, 1/2, 1, 3/2, \ldots)$

$$\boxed{\begin{array}{ll} \hat{M}_z Y = m_j\hbar Y & (m_j = -j, -j+1, \ldots, j-1, j) \\ \hat{M}^2 Y = j(j+1)\hbar^2 Y & (j = 0, 1/2, 1, 3/2, \ldots) \end{array}}$$

§3.3 多质点体系的角动量算符

The angular momenta of composite system

经典力学:

$$\vec{M}_t = \sum_n \vec{M}_n$$

总角动量$\boldsymbol{M_t}$等于每一质点角动量$\boldsymbol{M_n}$的矢量和

$$\vec{M}_n = \vec{i}M_{xn} + \vec{j}M_{yn} + \vec{k}M_{zn}$$

$$\vec{M}_t = \vec{i}M_{xt} + \vec{j}M_{yt} + \vec{k}M_{zt}$$

$$M_{xt} = \sum_n M_{xn} \quad M_{yt} = \sum_n M_{yn} \quad M_{zt} = \sum_n M_{zn}$$

$$\vec{M}_t \bullet \vec{M}_t = M_t^2 = M_{xt}^2 + M_{yt}^2 + M_{zt}^2$$

总角动量算符及对易规则

$$\hat{M}_{zt} = -i\hbar \sum_n \frac{\partial}{\partial \phi_n}$$

$$\left[\hat{M}_{xt}, \hat{M}_{yt}\right] = i\hbar \hat{M}_{zt} \quad \left[\hat{M}_{yt}, \hat{M}_{zt}\right] = i\hbar \hat{M}_{xt} \quad \left[\hat{M}_{zt}, \hat{M}_{xt}\right] = i\hbar \hat{M}_{yt}$$

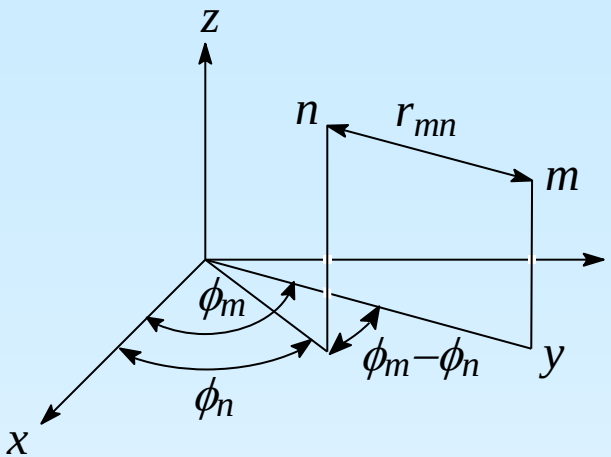
$$\left[\hat{M}_t^2, \hat{M}_{xt}\right] = \left[\hat{M}_t^2, \hat{M}_{yt}\right] = \left[\hat{M}_t^2, \hat{M}_{zt}\right] = 0$$

多电子原子中,不考虑自旋-轨道相互作用(原子单位)

$$\hat{H} = -\frac{1}{2}\sum_m \nabla_m^2 - \sum_m \frac{Z}{r_m} + \sum_{m>n}\sum \frac{1}{r_{mn}}$$

Laplace 算符∇^2中不包含ϕ_m, 只有$\partial^2/\partial\phi^2_m$，因此$\nabla^2$与$\hat{M}_{zt}$对易

下面看$1/r_{mn}$和$1/r_m$是否与$\hat{M}_{zt}$对易



$1/r_{mn}$是ϕ_m和ϕ_n差值$\Delta=\phi_m-\phi_n$的函数

$$\hat{M}_{zt}\frac{1}{r_{mn}}=\left(-i\hbar\sum\frac{\partial}{\partial\phi_m}\right)\frac{1}{r_{mn}}$$

$$=\frac{1}{r_{mn}}\left(-i\hbar\sum\frac{\partial}{\partial\phi_m}\right)-i\hbar\left[\frac{\partial(1/r_{mn})}{\partial\phi_m}+\frac{\partial(1/r_{mn})}{\partial\phi_n}\right]$$

$$=\frac{1}{r_{mn}}\hat{M}_{zt}-i\hbar\frac{d(1/r_{mn})}{d\Delta}\left(\frac{\partial\Delta}{\partial\phi_m}+\frac{\partial\Delta}{\partial\phi_n}\right)$$

$$=\frac{1}{r_{mn}}\hat{M}_{zt}$$

$1/r_{mn}$和$1/r_m$与 $\hat{M}_{zt}$ 对易

$$\boxed{\left[\hat{H},\hat{M}_{zt}\right]=0}$$

$$\left[\hat{H},\hat{M}_{zt}^2\right]=\left[\hat{H},\hat{M}_{zt}\right]\hat{M}_{zt}+\hat{M}_{zt}\left[\hat{H},\hat{M}_{zt}\right]=0$$

循环交换算符 $\hat{P}_c$

$$\hat{P}_c x = y \quad \hat{P}_c y = z \quad \hat{P}_c z = x \qquad \hat{P}_c \hat{H} \hat{P}_c^{-1} = \hat{H}$$

$$\hat{P}_c \left[\hat{H}, \hat{M}_{zt} \right] \hat{P}_c^{-1} = \left[\hat{H}, \hat{M}_{xt} \right] = 0$$

$$\hat{P}_c \left[\hat{H}, \hat{M}_{xt} \right] \hat{P}_c^{-1} = \left[\hat{H}, \hat{M}_{yt} \right] = 0$$

$$\hat{P}_c \left[\hat{H}, \hat{M}_{zt}^2 \right] \hat{P}_c^{-1} = \left[\hat{H}, \hat{M}_{xt}^2 \right] = 0$$

$$\hat{P}_c \left[\hat{H}, \hat{M}_{xt}^2 \right] \hat{P}_c^{-1} = \left[\hat{H}, \hat{M}_{yt}^2 \right] = 0$$

$$\boxed{\left[\hat{H}, \hat{M}_t^2 \right] = 0}$$

多电子原子的总能量、总角动量的平方和沿某一轴的分量可以同时有确定值(条件：自旋-轨道相互作用*spin-orbital interation*可以忽略不计)。

§3.4 电子自旋 Electron Spin

公设6 I 自旋算符均为Hermite算符，其对易规则与轨道角动量算符的对易规则相同。

单电子体系

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

$$\left[\hat{S}^2, \hat{S}_x\right] = 0 \quad \left[\hat{S}^2, \hat{S}_y\right] = 0 \quad \left[\hat{S}^2, \hat{S}_z\right] = 0$$

$$\left[\hat{S}_x, \hat{S}_y\right] = i\hbar\hat{S}_z \quad \left[\hat{S}_y, \hat{S}_z\right] = i\hbar\hat{S}_x \quad \left[\hat{S}_z, \hat{S}_x\right] = i\hbar\hat{S}_y$$

多电子体系

$$\hat{S}_t^2 = \hat{S}_{xt}^2 + \hat{S}_{yt}^2 + \hat{S}_{zt}^2$$

$$\hat{S}_{xt} = \sum_j \hat{S}_{xj} \quad \hat{S}_{yt} = \sum_j \hat{S}_{yj} \quad \hat{S}_{zt} = \sum_j \hat{S}_{zj}$$

$$\left[\hat{S}_t^2, \hat{S}_{xt}\right] = 0 \quad \left[\hat{S}_t^2, \hat{S}_{yt}\right] = 0 \quad \left[\hat{S}_t^2, \hat{S}_{zt}\right] = 0$$

$$\left[\hat{S}_{xt}, \hat{S}_{yt}\right] = i\hbar\hat{S}_{zt} \quad \left[\hat{S}_{yt}, \hat{S}_{zt}\right] = i\hbar\hat{S}_{xt} \quad \left[\hat{S}_{zt}, \hat{S}_{xt}\right] = i\hbar\hat{S}_{yt}$$

$$\hat{S}_t^2 Y = S(S+1)\hbar^2 Y \quad (S = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \ldots)$$

$$\hat{S}_{zt} Y = M_s \hbar Y \quad (M_s = -S, -S+1, \ldots, S-1, S)$$

公设6 II 单电子自旋算符的本征态与本征值

对单电子，$\hat{S}^2, \hat{S}_z$ 的本征态只有两个，分别用α和β表示

$$\hat{S}^2 \alpha = s(s+1)\hbar^2 \alpha = \frac{3}{4}\hbar^2 \alpha \quad \hat{S}_z \alpha = m_s \hbar \alpha = \frac{1}{2}\hbar \alpha$$

$$\hat{S}^2 \beta = s(s+1)\hbar^2 \beta = \frac{3}{4}\hbar^2 \beta \quad \hat{S}_z \beta = m_s \hbar \beta = -\frac{1}{2}\hbar \beta$$

自旋坐标为ω，通常说α和β是量子数m_s的函数 $\alpha = \alpha(m_s) \quad \beta = \beta(m_s)$

正交归一化条件 $\sum_{m_s=1/2}^{-1/2} |\alpha(m_s)|^2 = 1 \quad \sum_{m_s=1/2}^{-1/2} |\beta(m_s)|^2 = 1 \quad \sum_{m_s=1/2}^{-1/2} \alpha^*(m_s)\beta(m_s) = 0$

$$\alpha(m_s) = \delta_{m_s,1/2} \quad \beta(m_s) = \delta_{m_s,-1/2}$$

$$\alpha(1/2) = 1 \quad \alpha(-1/2) = 0 \quad \beta(1/2) = 0 \quad \beta(-1/2) = 1$$

公设6 III 自由电子的g因子

电子轨道运动角动量产生的磁矩

$$|\mu| = |M|\left(\frac{e}{2m_e c}\right) = \sqrt{l(l+1)}\hbar\left(\frac{e}{2m_e c}\right) = \sqrt{l(l+1)}\mu_B$$

$$\mu_B = \frac{e\hbar}{2m_e c} = 9.27402\times10^{-24}\,JT^{-1}$$ Bohr磁子

电子自旋角动量产生的磁矩

$$|\mu| = g_e\sqrt{s(s+1)}\hbar\left(\frac{e}{2m_e c}\right) = g_e\sqrt{s(s+1)}\mu_B$$

g_e 自由电子的Landé因子，g_e=2

电子自旋阶梯算符

$$\hat{S}_+ = \hat{S}_x + i\hat{S}_y$$

$$\hat{S}_- = \hat{S}_x - i\hat{S}_y$$

$$\hat{S}_+\hat{S}_- = \hat{S}^2 - \hat{S}_z^2 + \hbar\hat{S}_z$$

$$\hat{S}_-\hat{S}_+ = \hat{S}^2 - \hat{S}_z^2 - \hbar\hat{S}_z$$

$$\hat{S}_+\beta = \hbar\alpha$$

$$\hat{S}_-\alpha = \hbar\beta$$

$$\hat{S}_+\alpha = 0$$

$$\hat{S}_-\beta = 0$$

$$(\hat{S}_+ + \hat{S}_-)\beta = \hbar\alpha$$

$$(\hat{S}_+ - \hat{S}_-)\beta = \hbar\alpha$$

$$\Rightarrow \quad \hat{S}_x\beta = \frac{1}{2}\hbar\alpha$$

$$\hat{S}_y\beta = -\frac{1}{2}i\hbar\alpha$$

$$(\hat{S}_+ + \hat{S}_-)\alpha = \hbar\beta$$

$$(\hat{S}_+ - \hat{S}_-)\alpha = -\hbar\beta$$

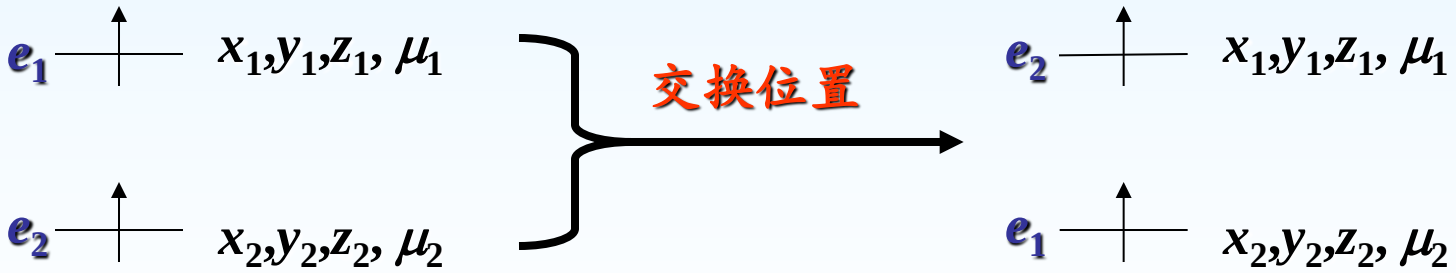
$$\Rightarrow \quad \hat{S}_x\alpha = \frac{1}{2}\hbar\beta$$

$$\hat{S}_y\alpha = \frac{1}{2}i\hbar\beta$$

§ 3.5 全同粒子体系与Pauli原理

3.5.1 全同粒子体系

- 全同粒子具有完全相同的内禀性质，如所有的电子具有相同的电荷、质量等，原子中的电子就构成一种全同粒子体系。
- 经典力学中，每个粒子有自己的轨道，因此虽然内禀性质相同，却可以区分，而在量子力学中，粒子具有波动性，只能得到粒子在各处出现的概率，无法确定是哪一个粒子
- 全同粒子体系中任意两个粒子交换时，不会造成任何可观测的后果



$\Psi(1,2)$ $\Psi(2,1)$

交换两个电子的位置，其概率状态不变

定义一个算符$\hat{P}_{ij}$，其作用为交换第i个和第j个粒子

$$\hat{P}_{ij}\psi(\cdots,i,\cdots,j,\cdots)=\psi(\cdots,j,\cdots,i,\cdots)$$

根据全同粒子的性质，$\psi(\ldots,i,\ldots,j,\ldots)$与$\psi(\ldots,j,\ldots,i,\ldots)$不能用任何观测手段加以区别，二者只相差一个因子$\lambda$

$$\hat{P}_{ij}\psi(\cdots,i,\cdots,j,\cdots)=\lambda\psi(\cdots,i,\cdots,j,\cdots)$$

$$\left.\begin{aligned}&\hat{P}_{ij}^2\psi(\cdots,i,\cdots,j,\cdots)=\lambda\hat{P}_{ij}\psi(\cdots,i,\cdots,j,\cdots)=\lambda^2\psi(\cdots,i,\cdots,j,\cdots)\\&\hat{P}_{ij}^2\psi(\cdots,i,\cdots,j,\cdots)=\psi(\cdots,i,\cdots,j,\cdots)\end{aligned}\right\}\ \lambda^2=1$$

$$\begin{cases}\hat{P}_{ij}\psi(\cdots,i,\cdots,j,\cdots)=\psi(\cdots,i,\cdots,j,\cdots) & \text{对称波函数}\\ \hat{P}_{ij}\psi(\cdots,i,\cdots,j,\cdots)=-\psi(\cdots,i,\cdots,j,\cdots) & \text{反对称波函数}\end{cases}$$

全同性粒子的完全波函数不是对称的，就是反对称的。

保里(Pauli)原理

多电子体系的总状态波函数一定是反对称的。

3.5.2 轨道近似，Slater行列式

独立粒子体系，粒子间没有相互作用

$$\hat{H}=\sum_{i}^{n}\hat{H}_i \qquad \hat{H}\Psi=E\Psi$$

令 $\Psi=\prod_{i}^{n}\psi_i \quad \Longrightarrow \quad \hat{H}_i\psi_i=E_i\psi_i$

实际粒子体系，粒子间存在相互作用，可通过设计成一种独立模型代替真正的多粒子体系。即将体系中每个粒子看成是在某种等效势场中与其他粒子无关地独立运动，每个粒子有自己的本征值和本征函数(单粒子态)，总波函数是单个粒子状态函数的积，这就是轨道近似(独立粒子近似)，独立粒子的本征函数也称为它的轨道。

$$\Psi^A(q_1,q_2,\ldots,q_N)=\frac{1}{\sqrt{N!}}\begin{vmatrix}\psi_1(q_1) & \psi_1(q_2) & \cdots & \psi_1(q_N)\\ \psi_2(q_1) & \psi_2(q_2) & \cdots & \psi_2(q_N)\\ \vdots & \vdots & & \vdots\\ \psi_N(q_1) & \psi_N(q_2) & \cdots & \psi_N(q_N)\end{vmatrix}$$

§3.6 原子角动量与光谱项

3.6.1 角动量的加和 Addition of angular momenta

设一个体系有两个角动量M_1和M_2，M_1和M_2可为是任何类型的两个角动量(两个轨道，两个自旋，一个轨道，一个自旋)

$\hat{M}_1^2, \hat{M}_2^2, \hat{M}_{z1}, \hat{M}_{z2}$ 本征值分别为$j_1(j_1+1)\hbar^2$，$j_2(j_2+1)\hbar^2$，$m_1\hbar$和$m_2\hbar$

$$\hat{M}_1^2 \left| j_1 m_1 \right\rangle = j_1(j_1+1)\hbar^2 \left| j_1 m_1 \right\rangle \qquad \hat{M}_{Z1} \left| j_1 m_1 \right\rangle = m_1\hbar \left| j_1 m_1 \right\rangle$$

$$\hat{M}_2^2 \left| j_2 m_2 \right\rangle = j_2(j_2+1)\hbar^2 \left| j_2 m_2 \right\rangle \qquad \hat{M}_{Z2} \left| j_2 m_2 \right\rangle = m_2\hbar \left| j_2 m_2 \right\rangle$$

$$\vec{M} = \vec{M}_1 + \vec{M}_2$$

$$\vec{M} = M_x\vec{i} + M_y\vec{j} + M_z\vec{k} \quad \Longrightarrow \quad \begin{aligned} M_x &= M_{1x} + M_{2x} \\ M_y &= M_{1y} + M_{2y} \\ M_z &= M_{1z} + M_{2z} \end{aligned}$$

$$\hat{M}^2 = \left(\hat{M}_1 + \hat{M}_2\right)\bullet\left(\hat{M}_1 + \hat{M}_2\right)$$
$$= \hat{M}_1^2 + \hat{M}_2^2 + \hat{M}_1\bullet\hat{M}_2 + \hat{M}_2\bullet\hat{M}_1$$
$$= \hat{M}_1^2 + \hat{M}_2^2 + 2\hat{M}_1\bullet\hat{M}_2$$
$$= \hat{M}_1^2 + \hat{M}_2^2 + 2(\hat{M}_{1x}\hat{M}_{2x} + \hat{M}_{1y}\hat{M}_{2y} + \hat{M}_{1z}\hat{M}_{2z})$$

$$\left[\hat{M}_x, \hat{M}_y\right] = \left[\hat{M}_{1x} + \hat{M}_{2x}, \hat{M}_{1y} + \hat{M}_{2y}\right]$$
$$= \left[\hat{M}_{1x}, \hat{M}_{1y}\right] + \left[\hat{M}_{1x}, \hat{M}_{2y}\right] + \left[\hat{M}_{2x}, \hat{M}_{1y}\right] + \left[\hat{M}_{2x}, \hat{M}_{2y}\right]$$
$$= \left[\hat{M}_{1x}, \hat{M}_{1y}\right] + \left[\hat{M}_{2x}, \hat{M}_{2y}\right]$$
$$= i\hbar\left(\hat{M}_{1z} + \hat{M}_{2z}\right) = i\hbar\hat{M}_z$$

$$\left[\hat{M}_x, \hat{M}_1^2\right] = \left[\hat{M}_y, \hat{M}_1^2\right] = \left[\hat{M}_z, \hat{M}_1^2\right] = \left[\hat{M}^2, \hat{M}_1^2\right] = 0$$
$$\left[\hat{M}_x, \hat{M}_2^2\right] = \left[\hat{M}_y, \hat{M}_2^2\right] = \left[\hat{M}_z, \hat{M}_2^2\right] = \left[\hat{M}^2, \hat{M}_2^2\right] = 0$$

$$\left[\hat{M}^2, \hat{M}_{1z}\right] \neq 0$$

$\hat{M}_1^2, \hat{M}_2^2, \hat{M}^2, \hat{M}_z$ 相互对易，可有共同的本征函数$|j_1 j_2 J M_J>$

将粒子1的完备集$|j_1m_1>$与粒子2的完备集$|j_2m_2>$相乘,得到两个粒子的完备波函数，每个未知的本征函数均可表示为

$$\left|j_1j_2JM_J\right\rangle=\sum c(j_1j_2JM_Jm_1m_2)\left|j_1m_1\right\rangle\left|j_2m_2\right\rangle$$

$|j_1j_2JM_J>$的本征值为

$\hat{M}_1^2$	$\hat{M}_2^2$	$\hat{M}^2$	$\hat{M}_z$
$j_1(j_1+1)\hbar^2$	$j_2(j_2+1)\hbar^2$	$J(J+1)\hbar^2$	$M_J\hbar$

$|j_1m_1>|j_2m_1>$是算符 $\hat{M}_1^2,\hat{M}_2^2,\hat{M}_{1z},\hat{M}_{2z}$ 的本征函数，其本征值为

$\hat{M}_1^2$	$\hat{M}_{1z}$	$\hat{M}_2^2$	$\hat{M}_{2z}$
$j_1(j_1+1)\hbar^2$	$m_1\hbar$	$j_2(j_2+1)\hbar^2$	$m_2\hbar$

$|j_1j_2JM_J>$，$|j_1m_1>|j_2m_2>$是 $\hat{M}_1^2$ 本征值为$j_1(j_1+1)\hbar^2$的本征函数，因此在展开式中只包括与$|j_1j_2JM_J>$具有相同j_1的项；同理只包括具有相同j_2的项。求和只遍及m_1、m_2的值。

先求M_J与m_1, m_2的关系

$$|j_1 j_2 J M_J\rangle = \sum \boxed{c(j_1 j_2 J M_J m_1 m_2)} |j_1 m_1\rangle |j_2 m_2\rangle$$

Clebsch-Gordan系数
Winger系数
矢量加和系数

$$\hat{M}_z = \hat{M}_{1z} + \hat{M}_{2z}$$

$$\hat{M}_z |j_1 j_2 J M_J\rangle = \sum c(j_1 j_2 J M_J m_1 m_2)\left(\hat{M}_{1z} + \hat{M}_{2z}\right)|j_1 m_1\rangle |j_2 m_2\rangle$$

$$M_J \hbar |j_1 j_2 J M_J\rangle = \sum c(j_1 j_2 J M_J m_1 m_2)(m_1\hbar + m_2\hbar)|j_1 m_1\rangle |j_2 m_2\rangle$$

$$\boxed{M_J = m_1 + m_2}$$

求J与j_1, j_2的关系

设j_1=1，j_2=2；m_1取值为–1,0,+1， m_2取值为–2, –1,0,+1,+2；用量子数j_1, j_2, m_1, m_2描述的体系，其微观状态数为$(2j_1+1)(2j_2+1)$=15，采用j_1, j_2, J, M_J描述，其微观状态数为15

M_J	+2	+1	0	–1	–2	$=m_2$
m_1= +1	+3	+2	+1	0	–1	
0	+2	+1	0	–1	–2	
–1	+1	0	–1	–2	–3	

M_J数值	+3	+2	+1	0	–1	–2	–3
出现次数	1	2	3	3	3	2	1

M_J从+3到–3，因此J的最大值一定是3，对于J=3，有7个M_J从+3到–3，去掉这7个，余下的是

M_J数值	+2	+1	0	–1	–2
出现次数	1	2	2	2	1

对应的J是2，对于J=2，有5个M_J从+2到–2，去掉这5个，余下

M_J数值	+1	0	–1
出现次数	1	1	1

显然对应的J是1，因此j_1=1和j_2=2，J的可能数值为3，2和1

- 考虑一般情况M_1和M_2的角量子数为j_1和j_2，因此其分别有$2j_1+1$个m_1的数值和$2j_2+1$个m_2的数值。因此有$(2j_1+1)(2j_2+1)$个可能的状态
- m_1的最高数值为j_1，m_2的最高数值为j_2，M_J的最高数值为j_1+j_2，M_J的取值是从J到$-J$，因此J的最高值一定是j_1+j_2
- M_J的次高数值为j_1+j_2-1，其来源有两个，即$m_1=j_1-1$，$m_2=j_2$和$m_1=j_1$，$m_2=j_2-1$；这两个状态的线性组合给出$J=j_1+j_2$，$M_J=j_1+j_2-1$的一个状态以及$J=j_1+j_2-1$，$M_J=j_1+j_2-1$的一个状态。依次继续，可求得的可能的J值为$j_1+j_2, j_1+j_2-1, j_1+j_2-2, \ldots, j_1+j_2-b$，$j_1+j_2-b$是$J$的最小数值。
- 对$J=j_1+j_2-k$，有$2(j_1+j_2-k)+1$个可能的M_J值

$$\sum_{k=0}^{b}\left[2(j_1+j_2-k)+1\right]=(2j_1+1)(2j_2+1) \Rightarrow b^2-2(j_1+j_2)b+4j_1j_2=0$$

$$\Downarrow$$

$$b=2j_1 \text{或} b=2j_2$$

$$J_{最小}=|j_1-j_2|$$

3.6.2 谱项及波函数

原子核的电荷为Z，核外电子数为N，在原子核固定并忽略核与电子体积时，多电子原子定态Schrödinger方程

$$\begin{cases} \hat{H}\Psi = E\Psi \\ \hat{H} = \hat{H}_0 + \hat{H}_m \end{cases}$$

$\hat{H}_m$ 代表磁相互作用，最重要的是旋轨耦合

$$\hat{H}_0\Psi = \sum_i \left[\left(-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i} \right) + \sum_{j<i} \frac{1}{r_{ij}} \right] \Psi$$

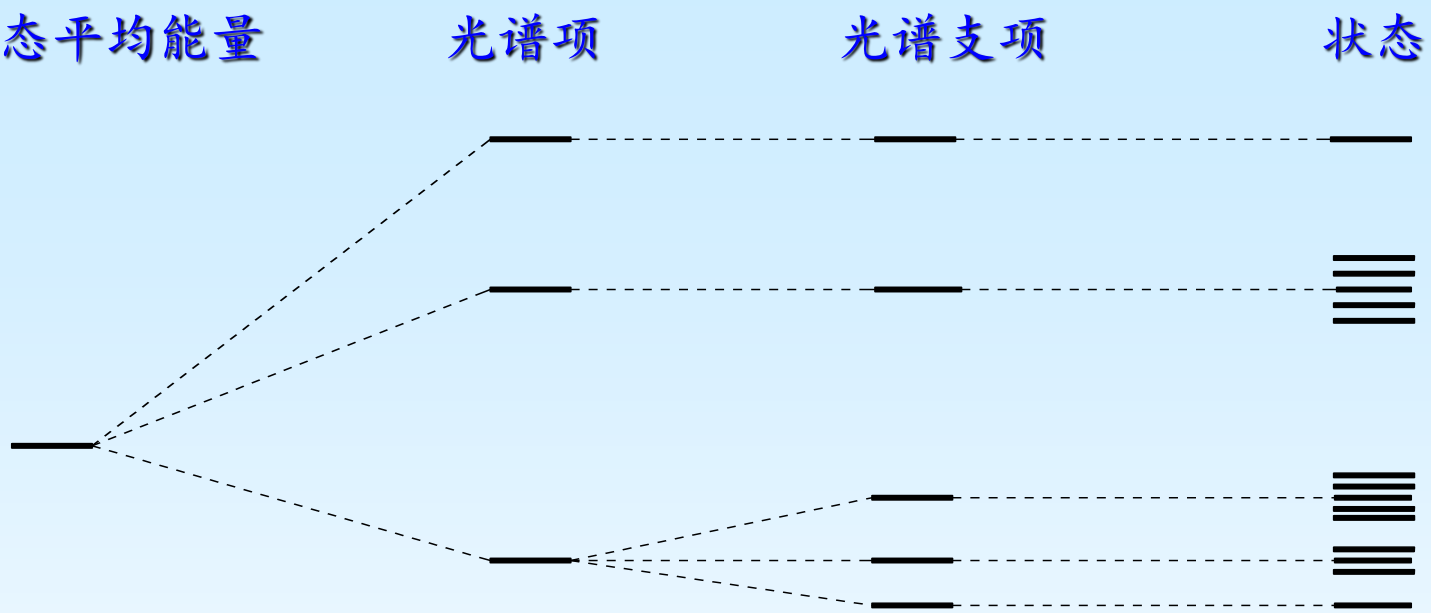
无法精确求解

$$\hat{H}_0 = \hat{H}_{00} + \hat{H}'$$

$$\hat{H}_{00} = \sum_i \left[-\frac{1}{2}\nabla_i^2 + V(r_i) \right]$$

$$\hat{H}' = \sum_i \left[\left(-V(r_i) - \frac{Z}{r_i} \right) + \sum_{j<i} \frac{1}{r_{ij}} \right]$$

$V(r_i)$为有效中心势场，如$V(r_i)$选择好，可以把 $\hat{H}'$ 当微扰项处理，这就是中心场近似



$\hat{H}_{00}$	$\hat{H}_{00}+\hat{H}'$	$\hat{H}_{00}+\hat{H}'+\hat{H}_{SO}$	$\hat{H}_{00}+\hat{H}'+\hat{H}_{SO}+\hat{H}_B$
中心势场	**电子瞬间作用**	**旋轨耦合作用**	**外磁场**
体系能量只与各电子的 ***n***和***l*** 有关	轨道角动量间 自旋角动量间	具有不同***J***的状态能级不同	蔡曼效应 不同J_z能级不同
组态 所有微观状态简并	***L, S***描述微观状态的能级	增加***J***描述微观状态的能级	增加J_z描述微观状态的能级

中心场无微扰态波函数**(零级近似波函数)**

$$\hat{H}_{00}\Psi_0=\left(\sum_i \hat{h}_i\right)\Psi_0=E_0\Psi_0 \qquad \hat{h}_i=-\frac{1}{2}\nabla_i^2+V(r_i)$$

$$\Psi_0(\boldsymbol{q}_1,\boldsymbol{q}_2,\cdots,\boldsymbol{q}_N)=\psi_1(\boldsymbol{q}_1)\psi_2(\boldsymbol{q}_2)\cdots\psi_N(\boldsymbol{q}_N)$$ **变量分离**

$$\hat{h}_i\psi_i(\boldsymbol{q}_i)=\varepsilon_i\psi_i(\boldsymbol{q}_i) \qquad E_0=\sum_{i=1}^{N}\varepsilon_i$$

$\boldsymbol{q}_i$表示第i个电子的坐标$\boldsymbol{r}_i$和自旋变量$\boldsymbol{\mu}_i$

$$\Downarrow$$

$$\psi_i(\boldsymbol{q}_i)=\psi_i(\boldsymbol{r}_i,\mu_i)=\phi_i(\boldsymbol{r}_i)\eta_i(\mu_i)=R_{n,l_i}(r_i)Y_{l_im_i}(\theta_i,\phi_i)\eta_i(\mu_i)$$

$\boldsymbol{\phi}_i(\boldsymbol{r}_i)$称为原子轨道，其$Y$与氢原子轨道的角度部分完全相同，径向部分是由$V(r_i)$决定的某种径向波函数；$\eta(\mu_i)$为自旋函数，$\boldsymbol{\psi}_i(\boldsymbol{q}_i)$称为**自旋轨道**，其有许多不同的表示方式，意义完全相同

$$\psi(\boldsymbol{q})\equiv\psi(\boldsymbol{r},\mu)\equiv|nlm_lm_s\rangle\equiv\psi_{nlm_l}\alpha(\text{或}\beta)\equiv nlm\alpha(\text{或}\beta)\equiv(m_l^{\pm})$$

中心场近似下，自旋轨道$\psi_i=|nlm_lm_s\rangle$的能量ε_i仅决定于n和l，与m_l,m_s无关，能量为ε_{nl}的自旋轨道有$2(2l+1)$个(简并度)。由(nl)决定的一组自旋轨道为nl亚层，如$n=2, l=1$(2p)亚层有6个自旋轨道，即$(1^+), (1^-), (0^+), (0^-), (-1^+), (-1^-)$，其能量均等于$\varepsilon_{2p}$，同一亚层的轨道称为等价轨道。

$(2p)^2$组态包含的15个微观状态

Φ_i	m_{l_1}	m_{l_2}	m_{s_1}	m_{s_2}	M_L	M_S	谱项
$\Phi_1=\Phi(1^+1^-)$	1	1	–½	½	2	0	^1D
$\Phi_2=\Phi(1^+0^+)$	1	0	½	½	1	1	^3P
$\Phi_3=\Phi(1^+0^-)$	1	0	½	–½	1	0	^1D, ^3P
$\Phi_4=\Phi(0^+1^-)$	0	1	½	–½	1	0	^1D, ^3P
$\Phi_5=\Phi(1^-0^-)$	1	0	–½	–½	1	–1	^3P
$\Phi_6=\Phi(1^+-1^+)$	1	–1	½	½	0	1	^3P
$\Phi_7=\Phi(1^+-1^-)$	1	–1	½	–½	0	0	^1D, ^3P,^1S
$\Phi_8=\Phi(0^+0^-)$	0	0	½	–½	0	0	^1D, ^3P,^1S
$\Phi_9=\Phi(-1^+1^-)$	–1	1	½	–½	0	0	^1D, ^3P,^1S
$\Phi_{10}=\Phi(1^--1^-)$	1	–1	–½	–½	0	–1	^3P
$\Phi_{11}=\Phi(-1^+0^+)$	–1	0	½	½	–1	1	^3P
$\Phi_{12}=\Phi(-1^+0^-)$	–1	0	½	–½	–1	0	^1D, ^3P
$\Phi_{13}=\Phi(0^+-1^-)$	0	–1	½	–½	–1	0	^1D, ^3P
$\Phi_{14}=\Phi(-1^-0^-)$	–1	0	–½	–½	–1	–1	^3P
$\Phi_{15}=\Phi(-1^+-1^-)$	–1	–1	½	–½	–2	0	^1D

Ψ_0并不满足Pauli原理的要求，因此需要写成Slater行列式的形式Φ，每一个Φ表示原子中电子运动的一个微观状态

$$\Phi = \frac{1}{\sqrt{N!}}\sum_p (-1)^p \hat{P}\psi_1(\boldsymbol{q}_1)\psi_2(\boldsymbol{q}_2)\cdots\psi_N(\boldsymbol{q}_N) \qquad E_0 = \sum_{i=1}^{N}\varepsilon_i$$

用电子在各个亚层中的分布来表示中心场近似下原子的电子结构，称为**电子组态(electronic configuration)**，如C原子基态的电子组态为$1s^2 2s^2 2p^2$，为简单起见，写电子组态时一般略去已充满的亚层，在微观状态的表示时也略去这些亚层中电子的坐标。

中心场近似采用$\boldsymbol{H}_{00}$得到的零级波函数，既无微扰态Φ_i和零级近似能量E_0不能解释由原子光谱得到的实验能级，因为组态能级还要分裂。如C原子的$E[(2p)^2]$要分裂为三组能级$E(^3P)$、$E(^1D)$和$E(^1S)$，这些能级组称为**光谱项**。采用$\boldsymbol{H}_0$和线性变分法可求得光谱项的能量和波函数。

L-S耦合与光谱项

多电子原子的一级近似(忽略旋轨耦合作用)的完备算符集合

$\hat{H}_0, \hat{L}^2, \hat{S}^2, \hat{L}_z, \hat{S}_z$

$$\hat{H}_0\Psi = E\Psi$$

$$\hat{L}^2\Psi = L(L+1)\Psi$$

$$\hat{S}^2\Psi = S(S+1)\Psi$$

$$\hat{L}_z\Psi = M_L\Psi$$

$$\hat{S}_z\Psi = M_S\Psi$$

原子单位

无微扰的Slater行列式波函数Φ是 $\hat{L}_z, \hat{S}_z$ 的本征函数

$$\hat{L}_z\Phi(l_1m_{l_1}m_{s_1}, l_2m_{l_2}m_{s_2}, \cdots l_Nm_{l_N}m_{s_N}) = M_L\Phi(l_1m_{l_1}m_{s_1}, l_2m_{l_2}m_{s_2}, \cdots l_Nm_{l_N}m_{s_N})$$

$$\hat{S}_z\Phi(l_1m_{l_1}m_{s_1}, l_2m_{l_2}m_{s_2}, \cdots l_Nm_{l_N}m_{s_N}) = M_S\Phi(l_1m_{l_1}m_{s_1}, l_2m_{l_2}m_{s_2}, \cdots l_Nm_{l_N}m_{s_N})$$

$$M_L = \sum_i m_{l_i} \qquad M_S = \sum_i m_{s_i}$$

闭壳层体系，Φ是 $\hat{L}^2, \hat{S}^2$ 的本征函数(L=S=0)，一般Φ不是 $\hat{L}^2, \hat{S}^2$ 本征函数，但两个算符作用在Φ上并不改变其M_L和M_S值，因此可以用具有相同M_L和M_S的行列式重新组成 $\hat{L}^2, \hat{S}^2, \hat{L}_z, \hat{S}_z$ 的共同本征函数

$(2p)^2$组态的15个微观状态中，M_L=2, M_S=0的状态只有一个，$\Phi(1^+1^-)$，其一定是 $\hat{L}^2, \hat{S}^2$ 的本征函数。

$$\Psi(LM_LSM_S) = \Psi(2200) \equiv \Phi(1^+1^-)$$

$$\left.\begin{aligned}
\Psi(2-200) &= \Phi(-1^+ -1^-) \\
\Psi(1111) &= \Phi(1^+0^+) \\
\Psi(111-1) &= \Phi(1^-0^-) \\
\Psi(1011) &= \Phi(1^+ -1^+) \\
\Psi(101-1) &= \Phi(1^- -1^-) \\
\Psi(1-111) &= \Phi(1^- -1^-) \\
\Psi(1-11-1) &= \Phi(-1^-0^-)
\end{aligned}\right\}$$

Φ_i	m_{l_1}	m_{l_2}	m_{s_1}	m_{s_2}	M_L	M_S	谱项
$\Phi_1=\Phi(1^+1^-)$	1	1	–½	½	2	0	^{1}D
$\Phi_2=\Phi(1^+0^+)$	1	0	½	½	1	1	^{3}P
$\Phi_5=\Phi(1^-0^-)$	1	0	–½	–½	1	–1	^{3}P
$\Phi_6=\Phi(1^+-1^+)$	1	–1	½	½	0	1	^{3}P
$\Phi_{10}=\Phi(1^--1^-)$	1	–1	–½	–½	0	–1	^{3}P
$\Phi_{11}=\Phi(-1^+0^+)$	–1	0	½	½	–1	1	^{3}P
$\Phi_{14}=\Phi(-1^-0^-)$	–1	0	–½	–½	–1	–1	^{3}P
$\Phi_{15}=\Phi(-1^+-1^-)$	–1	–1	½	–½	–2	0	^{1}D

M_L=1, M_S=0的微观状态有2个，可组合出L=1, S=1和L=2, S=0两个本征函数

$$\Psi(1110) = c_1\Phi(1^+0^-) + c_2\Phi(0^+1^-)$$

$$\Psi(2100) = c_3\Phi(1^+0^-) + c_4\Phi(0^+1^-)$$

同理

$$\Psi(1-110) = c_5\Phi(-1^+0^-) + c_6\Phi(0^+ -1^-)$$

$$\Psi(2-100) = c_7\Phi(-1^+0^-) + c_8\Phi(0^+ -1^-)$$

$$\Psi(1010) = c_9\Phi(1^+ -1^-) + c_{10}\Phi(0^+0^-) + c_{11}\Phi(-1^+1^-)$$

$$\Psi(2000) = c_{12}\Phi(1^+ -1^-) + c_{13}\Phi(0^+0^-) + c_{14}\Phi(-1^+1^-)$$

$$\Psi(0000) = c_{15}\Phi(1^+ -1^-) + c_{16}\Phi(0^+0^-) + c_{17}\Phi(-1^+1^-)$$

这样，就找到了$(2p)^2$电子组态的 $\hat{L}^2, \hat{S}^2, \hat{L}_z, \hat{S}_z$ 共同本征函数。

Φ_i	m_{l_1}	m_{l_2}	m_{s_1}	m_{s_2}	M_L	M_S	谱项
$\Phi_3=\Phi(1^+0^-)$	1	0	½	–½	1	0	^1D, ^3P
$\Phi_4=\Phi(0^+1^-)$	0	1	½	–½	1	0	^1D, ^3P
$\Phi_7=\Phi(1^+-1^-)$	1	–1	½	–½	0	0	^1D, ^3P,^1S
$\Phi_8=\Phi(0^+0^-)$	0	0	½	–½	0	0	^1D, ^3P,^1S
$\Phi_9=\Phi(-1^+1^-)$	–1	1	½	–½	0	0	^1D, ^3P,^1S
$\Phi_{12}=\Phi(-1^+0^-)$	–1	0	½	–½	–1	0	^1D, ^3P
$\Phi_{13}=\Phi(0^+-1^-)$	0	–1	½	–½	–1	0	^1D, ^3P

Russel-Saunder耦合方案

L-S耦合

3.6.3 阶梯算符求谱项的波函数

$$\hat{L}_{\pm} = \hat{L}_x + i\hat{L}_y \qquad \text{令} \quad \hat{L}_{\pm}\Psi(LM_L SM_S) = \Psi'$$

$$\hat{L}_z\Psi' = \hat{L}_z\hat{L}_{\pm}\Psi(LM_L SM_S) = \hat{L}_{\pm}\hat{L}_z\Psi(LM_L SM_S) \pm \hat{L}_{\pm}\Psi(LM_L SM_S)$$

$$= (M_L \pm 1)\hat{L}_{\pm}\Psi(LM_L SM_S) = (M_L \pm 1)\Psi'$$

$$\Psi' = c\Psi[L(M_L \pm 1)SM_S]$$

$$\langle\Psi'|\Psi'\rangle = |c|^2 = \left\langle \hat{L}_{\pm}\Psi(LM_L SM_S) \middle| \hat{L}_{\pm}\Psi(LM_L SM_S)\right\rangle$$

$$= \left\langle \Psi(LM_L SM_S) \middle| \hat{L}_{\mp}\hat{L}_{\pm}\Psi(LM_L SM_S)\right\rangle$$

$$\hat{L}_{\mp}\hat{L}_{\pm} = \hat{L}^2 - \hat{L}_z^2 \mp \hat{L}_z \qquad \hat{L}_{\mp}\hat{L}_{\pm}\Psi(LM_L SM_S) = [L(L+1) - M_L^2 \mp M_L]\Psi(LM_L SM_S)$$

$$|c|^2 = L(L+1) - M_L^2 \mp M_L$$

$$c = \sqrt{L(L+1) - M_L^2 \mp M_L} = \sqrt{(L \pm M_L + 1)(L \mp M_L)}$$

$$\hat{L}_{\pm}\Psi(LM_LSM_S)=\sqrt{(L\pm M_L+1)(L\mp M_L)}\Psi[L(M_L\pm 1)SM_S]$$

$$\hat{S}_{\pm}\Psi(LM_LSM_S)=\sqrt{(S\pm M_S+1)(S\mp M_S)}\Psi[LM_LS(M_s\pm 1)]$$

$$\hat{L}_{\pm}\Phi(l_1m_{l_1}m_{s_1},\cdots,l_Nm_{l_N}m_{s_N})=\sum_{k=1}^{N}\sqrt{(l_k\pm m_{l_k}+1)(l_k\mp m_{l_k})}$$

$$\times\Phi(l_1m_{l_1}m_{s_1},\cdots,l_k(m_{l_k}\pm 1)m_{s_k},\cdots,l_Nm_{l_N}m_{s_N})$$

$$\hat{S}_{\pm}\Phi(l_1m_{l_1}m_{s_1},\cdots,l_Nm_{l_N}m_{s_N})=\sum_{k=1}^{N}\sqrt{(\frac{3}{2}\pm m_{s_k})(\frac{1}{2}\mp m_{s_k})}$$

$$\times\Phi(l_1m_{l_1}m_{s_1},\cdots,l_km_{l_k}(m_{s_k}\pm 1),\cdots,l_Nm_{l_N}m_{s_N})$$

从最大的M_L(或M_S)值本征函数出发,用递降算符就可以得出属于该谱项的全部本征函数.如果有N个具有相同M_L,M_S值的无微扰函数Φ_i,在找出N–1个由它组成的本征函数Ψ_i后，第N个本征函数Ψ_N可利用正交关系求出。

d^2组态各谱项波函数的推导

d^2组态共45个状态，分属5个谱项^1G, ^3F, ^1D, ^3P, ^1S

^1G谱项　　$\Psi(4400)=\Phi(2^+2^-)$

$$\hat{L}_-\Psi(4400)=\sqrt{(4-4+1)(4+4)}\Psi(4300)=2\sqrt{2}\Psi(4300)$$

$$\hat{L}_-\Phi(2^+2^-)=\sqrt{(2-2+1)(2+2)}\Phi(1^+2^-)+\sqrt{(2-2+1)(2+2)}\Phi(2^+1^-)$$

$$=2\left[\Phi(1^+2^-)+\Phi(2^+1^-)\right]=2\left[\Phi(2^+1^-)-\Phi(2^-1^+)\right]$$

$$\Psi(4300)=\frac{1}{\sqrt{2}}\left[\Phi(2^+1^-)-\Phi(2^-1^+)\right]$$

$$\hat{L}_-\Psi(4300)=\sqrt{14}\Psi(4200)$$

$$\frac{1}{\sqrt{2}}\hat{L}_-\left[\Phi(1^+2^-)+\Phi(2^+1^-)\right]=\sqrt{3}\Phi(0^+2^-)+2\sqrt{2}\Phi(1^+1^-)+\sqrt{3}\Phi(2^+0^-)$$

$$\Psi(4200)=\frac{1}{\sqrt{14}}\left[\sqrt{3}\Phi(2^+0^-)+2\sqrt{2}\Phi(1^+1^-)-\sqrt{3}\Phi(2^-0^+)\right]$$

继续使用降算符可求出^1G的全部本征函数

^3F谱项M_L=3, M_S=1的态只有一个

$$\Psi(3311)=\Phi(2^+1^+)$$

$$\Psi(3211)=\Phi(2^+0^+)$$

$$\hat{L}_-\Psi(3311)=\sqrt{6}\Psi(3211)$$

$$\hat{L}_-\Phi(2^+1^+)=\cancel{2\Phi(1^+1^+)}+\sqrt{6}\Phi(2^+0^+)$$

$$\Psi(3211)=\Phi(2^+0^+)$$

$$\hat{S}_-\Psi(3211)=\sqrt{2}\Psi(3210)$$

$$\hat{S}_-\Phi(2^+0^+)=\Phi(2^-0^+)+\Phi(2^+0^-)$$

$$\Psi(3210)=\frac{1}{\sqrt{2}}\left[\Phi(2^-0^+)+\Phi(2^+0^-)\right]$$

继续使用降算符可求出^3F的全部本征函数

^1D谱项最大的M_L的本征态为$\Psi(2200)$， $M_L=2, M_S=0$的无微扰态有3个，$\Phi(2^+0^-)$, $\Phi(1^+1^-)$, $\Phi(2^-0^+)$, 因此

$$\Psi(2200)=c_1\Phi(2^+0^-)+c_2\Phi(1^+1^-)+c_3\Phi(2^-0^+)$$

$\Psi(2200)$与$\Psi(4200)$和$\Psi(3210)$相互正交

$$\langle\Psi(4200)|\Psi(2200)\rangle=\frac{1}{\sqrt{14}}(\sqrt{3}c_1+2\sqrt{2}c_2-\sqrt{3}c_3)=0$$

$$\langle\Psi(3210)|\Psi(2200)\rangle=\frac{1}{\sqrt{2}}(c_1+c_3)=0$$

$$c_3=-c_1$$

$$c_2=-\sqrt{\frac{3}{2}}c_1 \qquad \Psi(2200)=\frac{1}{\sqrt{7}}\left[\sqrt{2}\Phi(2^+0^-)-\sqrt{3}\Phi(1^+1^-)-\sqrt{2}\Phi(2^-0^+)\right]$$

继续使用相同的方法可以求出d^2组态全部谱项的本征函数