课堂练习

练习1：证明旋轨耦合中

$$|j = \tfrac{1}{2}, m = -\tfrac{1}{2}\rangle = \sqrt{\tfrac{1}{3}}|m_1 = 0, m_2 = -\tfrac{1}{2}\rangle - \sqrt{\tfrac{2}{3}}|m_1 = -1, m_2 = \tfrac{1}{2}\rangle$$

证明：首先，根据$m = m_1 + m_2$的耦合条件，只有满足$m_1 + m_2 = -\tfrac{1}{2}$的未耦合态前面的系数才不为0，此外$m_2 = \pm\tfrac{1}{2}$，因此可设$|j = \tfrac{1}{2}, m = -\tfrac{1}{2}\rangle = a|m_1 = 0, m_2 = -\tfrac{1}{2}\rangle + b|m_1 = -1, m_2 = \tfrac{1}{2}\rangle$，则由态矢的归一性，以及$|j = \tfrac{1}{2}, m = -\tfrac{1}{2}\rangle$与$|j = \tfrac{3}{2}, m = -\tfrac{1}{2}\rangle$的正交性（其中 $|j = \tfrac{3}{2}, m = -\tfrac{1}{2}\rangle = \sqrt{\tfrac{2}{3}}|m_1 = 0, m_2 = -\tfrac{1}{2}\rangle + \sqrt{\tfrac{1}{3}}|m_1 = -1, m_2 = \tfrac{1}{2}\rangle$），可得

$$\begin{cases} |a|^2 + |b|^2 = 1 \\ \sqrt{\tfrac{2}{3}}a + \sqrt{\tfrac{1}{3}}b = 0 \end{cases}, \text{解得} \begin{cases} a = \sqrt{\tfrac{1}{3}} \\ b = -\sqrt{\tfrac{2}{3}} \end{cases} \text{或} \begin{cases} a = -\sqrt{\tfrac{1}{3}} \\ b = \sqrt{\tfrac{2}{3}} \end{cases}，\text{不妨取}a\text{为正实数，则代入得}$$

$|j = \tfrac{1}{2}, m = -\tfrac{1}{2}\rangle = \sqrt{\tfrac{1}{3}}|m_1 = 0, m_2 = -\tfrac{1}{2}\rangle - \sqrt{\tfrac{2}{3}}|m_1 = -1, m_2 = \tfrac{1}{2}\rangle$，证毕

练习2：证明$\boldsymbol{R}_x(\varepsilon)\boldsymbol{R}_y(\varepsilon) - \boldsymbol{R}_y(\varepsilon)\boldsymbol{R}_x(\varepsilon) = \boldsymbol{R}_z(\varepsilon^2) - \boldsymbol{I}$

证明：根据定义，旋转矩阵展开至二阶项时的形式为：

$$\boldsymbol{R}_x(\varepsilon) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 - \tfrac{\varepsilon^2}{2} & -\varepsilon \\ 0 & \varepsilon & 1 - \tfrac{\varepsilon^2}{2} \end{bmatrix} \quad \boldsymbol{R}_y(\varepsilon) = \begin{bmatrix} 1 - \tfrac{\varepsilon^2}{2} & 0 & \varepsilon \\ 0 & 1 & 0 \\ -\varepsilon & 0 & 1 - \tfrac{\varepsilon^2}{2} \end{bmatrix} \quad \boldsymbol{R}_z(\varepsilon) = \begin{bmatrix} 1 - \tfrac{\varepsilon^2}{2} & -\varepsilon & 0 \\ \varepsilon & 1 - \tfrac{\varepsilon^2}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

作矩阵乘法得：

$$\boldsymbol{R}_x(\varepsilon)\boldsymbol{R}_y(\varepsilon) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 - \tfrac{\varepsilon^2}{2} & -\varepsilon \\ 0 & \varepsilon & 1 - \tfrac{\varepsilon^2}{2} \end{bmatrix} \begin{bmatrix} 1 - \tfrac{\varepsilon^2}{2} & 0 & \varepsilon \\ 0 & 1 & 0 \\ -\varepsilon & 0 & 1 - \tfrac{\varepsilon^2}{2} \end{bmatrix} = \begin{bmatrix} 1 - \tfrac{\varepsilon^2}{2} & 0 & \varepsilon \\ \varepsilon^2 & 1 - \tfrac{\varepsilon^2}{2} & -\varepsilon(1 - \tfrac{\varepsilon^2}{2}) \\ -\varepsilon(1 - \tfrac{\varepsilon^2}{2}) & \varepsilon & (1 - \tfrac{\varepsilon^2}{2})^2 \end{bmatrix}$$

$$\boldsymbol{R}_y(\varepsilon)\boldsymbol{R}_x(\varepsilon) = \begin{bmatrix} 1 - \tfrac{\varepsilon^2}{2} & 0 & \varepsilon \\ 0 & 1 & 0 \\ -\varepsilon & 0 & 1 - \tfrac{\varepsilon^2}{2} \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 - \tfrac{\varepsilon^2}{2} & -\varepsilon \\ 0 & \varepsilon & 1 - \tfrac{\varepsilon^2}{2} \end{bmatrix} = \begin{bmatrix} 1 - \tfrac{\varepsilon^2}{2} & \varepsilon^2 & \varepsilon(1 - \tfrac{\varepsilon^2}{2}) \\ 0 & 1 - \tfrac{\varepsilon^2}{2} & -\varepsilon \\ -\varepsilon & \varepsilon(1 - \tfrac{\varepsilon^2}{2}) & (1 - \tfrac{\varepsilon^2}{2})^2 \end{bmatrix}$$

两项相减，并忽略三次及更高次项，得：

$$\boldsymbol{R}_x(\varepsilon)\boldsymbol{R}_y(\varepsilon) - \boldsymbol{R}_y(\varepsilon)\boldsymbol{R}_x(\varepsilon) = \begin{bmatrix} 0 & -\varepsilon^2 & \tfrac{\varepsilon^3}{2} \\ \varepsilon^2 & 0 & \tfrac{\varepsilon^3}{2} \\ \tfrac{\varepsilon^3}{2} & \tfrac{\varepsilon^3}{2} & 0 \end{bmatrix} \simeq \begin{bmatrix} 0 & -\varepsilon^2 & 0 \\ \varepsilon^2 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

又

$$\boldsymbol{R}_z(\varepsilon^2) - \boldsymbol{I} = \begin{bmatrix} 1 - \tfrac{\varepsilon^4}{2} & -\varepsilon^2 & 0 \\ \varepsilon^2 & 1 - \tfrac{\varepsilon^4}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} - \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} -\tfrac{\varepsilon^4}{2} & -\varepsilon^2 & 0 \\ \varepsilon^2 & -\tfrac{\varepsilon^4}{2} & 0 \\ 0 & 0 & 0 \end{bmatrix} \simeq \begin{bmatrix} 0 & -\varepsilon^2 & 0 \\ \varepsilon^2 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

因此$\boldsymbol{R}_x(\varepsilon)\boldsymbol{R}_y(\varepsilon) - \boldsymbol{R}_y(\varepsilon)\boldsymbol{R}_x(\varepsilon) = \boldsymbol{R}_z(\varepsilon^2) - \boldsymbol{I}$，原题得证

练习3：是否有其他方式来推导$e^{-\tfrac{i}{\hbar}\boldsymbol{S}_y\theta} = \begin{pmatrix} \cos\tfrac{\theta}{2} & -\sin\tfrac{\theta}{2} \\ \sin\tfrac{\theta}{2} & \cos\tfrac{\theta}{2} \end{pmatrix}$？

解:

练习4：请用贝克-豪斯多夫公式推导$\mathrm{e}^{\frac{\mathrm{i}}{\hbar}\hat{S}_z\phi}\hat{S}_x\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}\hat{S}_z\phi}=\hat{S}_x\cos\phi-\hat{S}_y\sin\phi$

解：首先我们要推导$\underbrace{[\frac{\mathrm{i}}{\hbar}\hat{S}_z\phi,[\ldots,[\frac{\mathrm{i}}{\hbar}\hat{S}_z\phi,\hat{S}_x]]]}_{k层对易符号}$的表达式，显然对易符号只有一层时，有

$[\frac{\mathrm{i}}{\hbar}\hat{S}_z\phi,\hat{S}_x]=\frac{\mathrm{i}\phi}{\hbar}[\hat{S}_z,\hat{S}_x]=\frac{\mathrm{i}\phi}{\hbar}\cdot\mathrm{i}\hbar\hat{S}_y=-\phi\hat{S}_y$；对易符号有两层时，有

$[\frac{\mathrm{i}}{\hbar}\hat{S}_z\phi,[\frac{\mathrm{i}}{\hbar}\hat{S}_z\phi,\hat{S}_x]]=[\frac{\mathrm{i}}{\hbar}\hat{S}_z\phi,-\phi\hat{S}_y]=-\frac{\mathrm{i}\phi^2}{\hbar}[\hat{S}_z,\hat{S}_y]=-\frac{\mathrm{i}\phi^2}{\hbar}\cdot(-\mathrm{i}\hbar\hat{S}_x)=-\phi^2\hat{S}_x$，因此我们可以

猜想，当$k=2p+1$时，有$\underbrace{[\frac{\mathrm{i}}{\hbar}\hat{S}_z\phi,[\ldots,[\frac{\mathrm{i}}{\hbar}\hat{S}_z\phi,\hat{S}_x]]]}_{(2p+1)层对易符号}=(-1)^{p+1}\phi^{2p+1}\hat{S}_y$；当$k=2p$时，有

$\underbrace{[\frac{\mathrm{i}}{\hbar}\hat{S}_z\phi,[\ldots,[\frac{\mathrm{i}}{\hbar}\hat{S}_z\phi,\hat{S}_x]]]}_{2p层对易符号}=(-1)^p\phi^{2p}\hat{S}_x$，其中$p\in\mathbb{N}$。这两个均可以采用数学归纳法证明：以奇数

情形为例，假设$k=2q+1\ (q\in\mathbb{N})$时成立，则当$k=2(q+1)+1=2q+3$时，有：

$$\underbrace{[\frac{\mathrm{i}}{\hbar}\hat{S}_z\phi,[\ldots,[\frac{\mathrm{i}}{\hbar}\hat{S}_z\phi,\hat{S}_x]]]}_{(2q+3)层对易符号}=[\frac{\mathrm{i}}{\hbar}\hat{S}_z\phi,[\frac{\mathrm{i}}{\hbar}\hat{S}_z\phi,(-1)^{q+1}\phi^{2p+1}\hat{S}_y]]=[\frac{\mathrm{i}}{\hbar}\hat{S}_z\phi,(-1)^{q+1}\phi^{2p+1}\cdot(\frac{\mathrm{i}\phi}{\hbar})[\hat{S}_z,\hat{S}_y]]$$

$$=[\frac{\mathrm{i}}{\hbar}\hat{S}_z\phi,(-1)^{q+1}\phi^{2p+1}\cdot(\frac{\mathrm{i}\phi}{\hbar})\cdot(-\mathrm{i}\hbar\hat{S}_x)]=\frac{\mathrm{i}\phi}{\hbar}(-1)^{q+1}\phi^{2p+1}\cdot(\frac{\mathrm{i}\phi}{\hbar})\cdot(-\mathrm{i}\hbar)[\hat{S}_z,\hat{S}_x]$$

$$=\frac{\mathrm{i}\phi}{\hbar}(-1)^{q+1}\phi^{2p+1}\cdot(\frac{\mathrm{i}\phi}{\hbar})\cdot(-\mathrm{i}\hbar)\cdot(\mathrm{i}\hbar\hat{S}_y)=(-1)^{q+2}\phi^{2p+3}\hat{S}_y$$

此法对偶数情形亦成立。接下来，利用贝克-豪斯多夫公式，我们得到：

$$\mathrm{e}^{\frac{\mathrm{i}}{\hbar}\hat{S}_z\phi}\hat{S}_x\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}\hat{S}_z\phi}=\sum_{k=0}^{\infty}\frac{1}{k!}\underbrace{[\frac{\mathrm{i}}{\hbar}\hat{S}_z\phi,[\ldots,[\frac{\mathrm{i}}{\hbar}\hat{S}_z\phi,\hat{S}_x]]]}_{k层对易符号}=\sum_{k_1=0}^{\infty}\frac{(-1)^{k_1+1}\phi^{2k_1+1}\hat{S}_y}{(2k_1+1)!}+\sum_{k_2=0}^{\infty}\frac{(-1)^{k_2}\phi^{2k_2}\hat{S}_x}{(2k_2)!}$$

$$=-\sum_{k_1=0}^{\infty}[\frac{d^{k_1}(\sin\theta)}{d\theta^{k_1}}]_{\theta=0}\frac{(\phi-0)^{k_1}}{k_1!}\hat{S}_y+\sum_{k_2=0}^{\infty}[\frac{d^{k_2}(\cos\theta)}{d\theta^{k_2}}]_{\theta=0}\frac{(\phi-0)^{k_2}}{k_2!}\hat{S}_x=-\hat{S}_y\sin\phi+\hat{S}_x\cos\phi$$

第四章习题

4.1 用直接计算在$|S_z\pm\rangle$上表示的矩阵元的方法验证4.3.5和4.3.6式，即

$$S_x=\frac{\hbar}{2}\begin{pmatrix}0&1\\1&0\end{pmatrix}\quad S_y=\frac{\hbar}{2}\begin{pmatrix}0&-\mathrm{i}\\\mathrm{i}&0\end{pmatrix}\quad S_z=\frac{\hbar}{2}\begin{pmatrix}1&0\\0&-1\end{pmatrix}\quad S_+=\hbar\begin{pmatrix}0&1\\0&0\end{pmatrix}\quad S_-=\hbar\begin{pmatrix}0&0\\1&0\end{pmatrix}$$

4.2 在坐标空间表象中，$\hat{L}_z,\hat{L}^2$的本征函数是球谐函数，在动量空间表象中，$\hat{L}_z,\hat{L}^2$的本征函数是什么？

解：可以证明，在动量空间表象中，$\hat{L}_z,\hat{L}^2$的本征函数仍然是球谐函数，证明如下：
设在位置空间表象中，任意波函数可表示为$\psi(\boldsymbol{r})=\psi(r,\theta,\varphi)=f(r)Y_L^M(\theta,\varphi)$，则经傅里叶变换后，波函数在动量空间表象的形式为：

$$\widetilde{\psi}(\boldsymbol{p})=(2\pi)^{-\frac{3}{2}}\iiint\mathrm{e}^{-\mathrm{i}\boldsymbol{p}\cdot\boldsymbol{r}}f(r)Y_L^M(\theta,\varphi)r^2\sin\theta drd\varphi d\theta$$

又平面波按球谐函数展开之后为：

$$\mathrm{e}^{-\mathrm{i}\boldsymbol{p}\cdot\boldsymbol{r}}=4\pi\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\mathrm{e}^{-\frac{\mathrm{i}\pi l}{2}}j_l(kr)[Y_l^m(\theta,\varphi)]^*Y_l^m(\theta_p,\varphi_p)$$

因此代入得

$$\widetilde{\psi}(\boldsymbol{p}) = (2\pi)^{-\frac{3}{2}} \int r^2 dr \iint 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \mathrm{e}^{-\frac{\mathrm{i}\pi l}{2}} j_l(kr) [Y_l^m(\theta,\varphi)]^* Y_l^m(\theta_p,\varphi_p) f(r) Y_L^M(\theta,\varphi) \sin\theta d\varphi d\theta$$

$$= \sqrt{\frac{2}{\pi}} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \mathrm{e}^{-\frac{\mathrm{i}\pi l}{2}} Y_l^m(\theta_p,\varphi_p) \int r^2 j_l(pr) f(r) dr \iint [Y_l^m(\theta,\varphi)]^* Y_L^M(\theta,\varphi) \sin\theta d\varphi d\theta$$

$$= \sqrt{\frac{2}{\pi}} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \mathrm{e}^{-\frac{\mathrm{i}\pi l}{2}} Y_l^m(\theta_p,\varphi_p) \int r^2 j_l(pr) f(r) \delta_{mM} \delta_{lL} dr = \sqrt{\frac{2}{\pi}} \mathrm{e}^{-\frac{\mathrm{i}\pi L}{2}} Y_L^M(\theta_p,\varphi_p) \int r^2 j_l(pr) f(r) dr$$

从而在动量空间表象中，$\hat{L}_z, \hat{L}^2$ 的本征函数仍然是球谐函数

4.3 两个电子自旋耦合相互作用的哈密顿算符为 $\hat{H} = A\hat{\boldsymbol{S}}_1 \cdot \hat{\boldsymbol{S}}_2$，式中A为常数。求出 $\hat{H} = A\hat{\boldsymbol{S}}_1 \cdot \hat{\boldsymbol{S}}_2$，$\hat{\boldsymbol{S}}^2 = (\hat{\boldsymbol{S}}_1 + \hat{\boldsymbol{S}}_2)^2$，$\hat{S}_z = \hat{S}_{z,1} + \hat{S}_{z,2}$ 用未耦合表象基组表示的共同本征矢和相应的本征值，每一个能级简并度是多少？它们关于两个电子交换的对称性如何？

解：记两电子未耦合表象为 $|\frac{1}{2}, m_{s,1}; \frac{1}{2}, m_{s,2}\rangle \equiv |\sigma_1\sigma_2\rangle$，其中 $\sigma_1, \sigma_2 = \alpha, \beta$，则对 $\hat{S}_z = \hat{S}_{z,1} + \hat{S}_{z,2}$，其作用在未耦合表象的效果为：

$$\begin{cases} \hat{S}_z|\alpha\alpha\rangle = (\hat{S}_{z,1} + \hat{S}_{z,2})|\alpha\alpha\rangle = \hat{S}_{z,1}|\alpha\alpha\rangle + \hat{S}_{z,2}|\alpha\alpha\rangle = \frac{\hbar}{2}|\alpha\alpha\rangle + \frac{\hbar}{2}|\alpha\alpha\rangle = \hbar|\alpha\alpha\rangle \\ \hat{S}_z|\alpha\beta\rangle = (\hat{S}_{z,1} + \hat{S}_{z,2})|\alpha\beta\rangle = \hat{S}_{z,1}|\alpha\beta\rangle + \hat{S}_{z,2}|\alpha\beta\rangle = \frac{\hbar}{2}|\alpha\beta\rangle - \frac{\hbar}{2}|\alpha\beta\rangle = \mathbf{0} \\ \hat{S}_z|\beta\alpha\rangle = (\hat{S}_{z,1} + \hat{S}_{z,2})|\beta\alpha\rangle = \hat{S}_{z,1}|\beta\alpha\rangle + \hat{S}_{z,2}|\beta\alpha\rangle = -\frac{\hbar}{2}|\beta\alpha\rangle + \frac{\hbar}{2}|\beta\alpha\rangle = \mathbf{0} \\ \hat{S}_z|\beta\beta\rangle = (\hat{S}_{z,1} + \hat{S}_{z,2})|\beta\beta\rangle = \hat{S}_{z,1}|\beta\beta\rangle + \hat{S}_{z,2}|\beta\beta\rangle = -\frac{\hbar}{2}|\beta\beta\rangle - \frac{\hbar}{2}|\beta\beta\rangle = -\hbar|\beta\beta\rangle \end{cases}$$

因此 $\hat{S}_z$ 在未耦合表象上的矩阵为 $\boldsymbol{S}_z = \hbar \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$，

接下来是 $\hat{H} = A\hat{\boldsymbol{S}}_1 \cdot \hat{\boldsymbol{S}}_2$，显然由于

$$\hat{\boldsymbol{S}}_1 \cdot \hat{\boldsymbol{S}}_2 = \hat{S}_{1,x}\hat{S}_{2,x} + \hat{S}_{1,y}\hat{S}_{2,y} + \hat{S}_{1,z}\hat{S}_{2,z} = \frac{1}{2}(\hat{S}_{1,+} + \hat{S}_{1,-}) \cdot \frac{1}{2}(\hat{S}_{2,+} + \hat{S}_{2,-}) + \frac{1}{2\mathrm{i}}(\hat{S}_{1,+} - \hat{S}_{1,-}) \cdot \frac{1}{2\mathrm{i}}(\hat{S}_{2,+} - \hat{S}_{2,-}) + \hat{S}_{1,z}\hat{S}_{2,z}$$

$$= \frac{1}{2}(\hat{S}_{1,+}\hat{S}_{2,-} + \hat{S}_{1,-}\hat{S}_{2,+}) + \hat{S}_{1,z}\hat{S}_{2,z}$$

因此 $\hat{H}$ 作用在未耦合表象的效果为：

$$\begin{cases} \hat{H}|\alpha\alpha\rangle = A[\frac{1}{2}(\hat{S}_{1,+}\hat{S}_{2,-} + \hat{S}_{1,-}\hat{S}_{2,+}) + \hat{S}_{1,z}\hat{S}_{2,z}]|\alpha\alpha\rangle = \frac{A}{2}\hat{S}_{1,+}\hat{S}_{2,-}|\alpha\alpha\rangle + \frac{A}{2}\hat{S}_{1,-}\hat{S}_{2,+}|\alpha\alpha\rangle + A\hat{S}_{1,z}\hat{S}_{2,z}|\alpha\alpha\rangle = \frac{A\hbar^2}{4}|\alpha\alpha\rangle \\ \hat{H}|\alpha\beta\rangle = A[\frac{1}{2}(\hat{S}_{1,+}\hat{S}_{2,-} + \hat{S}_{1,-}\hat{S}_{2,+}) + \hat{S}_{1,z}\hat{S}_{2,z}]|\alpha\beta\rangle = \frac{A}{2}\hat{S}_{1,+}\hat{S}_{2,-}|\alpha\beta\rangle + \frac{A}{2}\hat{S}_{1,-}\hat{S}_{2,+}|\alpha\beta\rangle + A\hat{S}_{1,z}\hat{S}_{2,z}|\alpha\beta\rangle = \frac{A\hbar^2}{2}|\beta\alpha\rangle - \frac{A\hbar^2}{4}|\alpha\beta\rangle \\ \hat{H}|\beta\alpha\rangle = A[\frac{1}{2}(\hat{S}_{1,+}\hat{S}_{2,-} + \hat{S}_{1,-}\hat{S}_{2,+}) + \hat{S}_{1,z}\hat{S}_{2,z}]|\beta\alpha\rangle = \frac{A}{2}\hat{S}_{1,+}\hat{S}_{2,-}|\beta\alpha\rangle + \frac{A}{2}\hat{S}_{1,-}\hat{S}_{2,+}|\beta\alpha\rangle + A\hat{S}_{1,z}\hat{S}_{2,z}|\beta\alpha\rangle = \frac{A\hbar^2}{2}|\alpha\beta\rangle - \frac{A\hbar^2}{4}|\beta\alpha\rangle \\ \hat{H}|\beta\beta\rangle = A[\frac{1}{2}(\hat{S}_{1,+}\hat{S}_{2,-} + \hat{S}_{1,-}\hat{S}_{2,+}) + \hat{S}_{1,z}\hat{S}_{2,z}]|\beta\beta\rangle = \frac{A}{2}\hat{S}_{1,+}\hat{S}_{2,-}|\beta\beta\rangle + \frac{A}{2}\hat{S}_{1,-}\hat{S}_{2,+}|\beta\beta\rangle + A\hat{S}_{1,z}\hat{S}_{2,z}|\beta\beta\rangle = \frac{A\hbar^2}{4}|\beta\beta\rangle \end{cases}$$

从而 $\hat{H}$ 在未耦合表象上的矩阵为 $\boldsymbol{H} = \frac{A\hbar^2}{4} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 2 & 0 \\ 0 & 2 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$

最后是 $\hat{\boldsymbol{S}}^2 = (\hat{\boldsymbol{S}}_1 + \hat{\boldsymbol{S}}_2)^2$，变形得：

$$\hat{\boldsymbol{S}}^2 = (\hat{\boldsymbol{S}}_1 + \hat{\boldsymbol{S}}_2)^2 = \hat{\boldsymbol{S}}_1^2 + \hat{\boldsymbol{S}}_2^2 + \hat{\boldsymbol{S}}_1 \cdot \hat{\boldsymbol{S}}_2 + \hat{\boldsymbol{S}}_2 \cdot \hat{\boldsymbol{S}}_1$$

$$= \hat{\boldsymbol{S}}_1^2 + \hat{\boldsymbol{S}}_2^2 + \frac{1}{2}(\hat{S}_{1,+}\hat{S}_{2,-} + \hat{S}_{1,-}\hat{S}_{2,+}) + \hat{S}_{1,z}\hat{S}_{2,z} + \frac{1}{2}(\hat{S}_{2,+}\hat{S}_{1,-} + \hat{S}_{2,-}\hat{S}_{1,+}) + \hat{S}_{2,z}\hat{S}_{1,z}$$

$$= \hat{\boldsymbol{S}}_1^2 + \hat{\boldsymbol{S}}_2^2 + \hat{S}_{1,+}\hat{S}_{2,-} + \hat{S}_{1,-}\hat{S}_{2,+} + 2\hat{S}_{1,z}\hat{S}_{2,z} \text{（利用不同电子的自旋算符满足交换律）}$$

因此 $\hat{\boldsymbol{S}}^2$ 作用在未耦合表象的效果为：

$$\begin{cases} \hat{\boldsymbol{S}}^2|\alpha\alpha\rangle = (\hat{\boldsymbol{S}}_1^2 + \hat{\boldsymbol{S}}_2^2 + \hat{S}_{1,+}\hat{S}_{2,-} + \hat{S}_{1,-}\hat{S}_{2,+} + 2\hat{S}_{1,z}\hat{S}_{2,z})|\alpha\alpha\rangle = 2\hbar^2|\alpha\alpha\rangle \\ \hat{\boldsymbol{S}}^2|\alpha\beta\rangle = (\hat{\boldsymbol{S}}_1^2 + \hat{\boldsymbol{S}}_2^2 + \hat{S}_{1,+}\hat{S}_{2,-} + \hat{S}_{1,-}\hat{S}_{2,+} + 2\hat{S}_{1,z}\hat{S}_{2,z})|\alpha\beta\rangle = \hbar^2|\alpha\beta\rangle + \hbar^2|\beta\alpha\rangle \\ \hat{\boldsymbol{S}}^2|\beta\alpha\rangle = (\hat{\boldsymbol{S}}_1^2 + \hat{\boldsymbol{S}}_2^2 + \hat{S}_{1,+}\hat{S}_{2,-} + \hat{S}_{1,-}\hat{S}_{2,+} + 2\hat{S}_{1,z}\hat{S}_{2,z})|\beta\alpha\rangle = \hbar^2|\beta\alpha\rangle + \hbar^2|\alpha\beta\rangle \\ \hat{\boldsymbol{S}}^2|\beta\beta\rangle = (\hat{\boldsymbol{S}}_1^2 + \hat{\boldsymbol{S}}_2^2 + \hat{S}_{1,+}\hat{S}_{2,-} + \hat{S}_{1,-}\hat{S}_{2,+} + 2\hat{S}_{1,z}\hat{S}_{2,z})|\beta\beta\rangle = 2\hbar^2|\beta\beta\rangle \end{cases}$$

从而$\hat{\boldsymbol{S}}^2$在未耦合表象上的矩阵为$\boldsymbol{S}^2 = \hbar^2 \begin{pmatrix} 2 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 2 \end{pmatrix}$

现在我们回到本题，设耦合表象的态矢可表示为$|ab\rangle = c_{\alpha\alpha}|\alpha\alpha\rangle + c_{\alpha\beta}|\alpha\beta\rangle + c_{\beta\alpha}|\beta\alpha\rangle + c_{\beta\beta}|\beta\beta\rangle$，其中$|c_{\alpha\alpha}|^2 + |c_{\alpha\beta}|^2 + |c_{\beta\alpha}|^2 + |c_{\beta\beta}|^2 = 1$；$a, b$分别与$\hat{\boldsymbol{S}}^2, \hat{S}_z$作用在耦合表象的态矢时得到的本征值有关：$\hat{\boldsymbol{S}}^2|ab\rangle = a(a+1)\hbar^2|ab\rangle \equiv R\hbar^2|ab\rangle$，$\hat{S}_z|ab\rangle = b\hbar|ab\rangle \equiv S\hbar|ab\rangle$，$\hat{H}|ab\rangle \equiv T\hbar^2|ab\rangle$，且$a > 0$。则分别乘未耦合表象的基矢，并插入单位算符，得：

$$\hbar^2 \begin{pmatrix} 2 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 2 \end{pmatrix} \begin{pmatrix} c_{\alpha\alpha} \\ c_{\alpha\beta} \\ c_{\beta\alpha} \\ c_{\beta\beta} \end{pmatrix} = R\hbar^2 \begin{pmatrix} c_{\alpha\alpha} \\ c_{\alpha\beta} \\ c_{\beta\alpha} \\ c_{\beta\beta} \end{pmatrix}$$

$$\hbar \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} c_{\alpha\alpha} \\ c_{\alpha\beta} \\ c_{\beta\alpha} \\ c_{\beta\beta} \end{pmatrix} = S\hbar \begin{pmatrix} c_{\alpha\alpha} \\ c_{\alpha\beta} \\ c_{\beta\alpha} \\ c_{\beta\beta} \end{pmatrix}$$

$$\frac{A\hbar^2}{4} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 2 & 0 \\ 0 & 2 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} c_{\alpha\alpha} \\ c_{\alpha\beta} \\ c_{\beta\alpha} \\ c_{\beta\beta} \end{pmatrix} = T\hbar^2 \begin{pmatrix} c_{\alpha\alpha} \\ c_{\alpha\beta} \\ c_{\beta\alpha} \\ c_{\beta\beta} \end{pmatrix}$$

相应的久期方程为：

$$\begin{vmatrix} 2-R & 0 & 0 & 0 \\ 0 & 1-R & 1 & 0 \\ 0 & 1 & 1-R & 0 \\ 0 & 0 & 0 & 2-R \end{vmatrix} = R(R-2)^3 = 0$$

$$\begin{vmatrix} 1-S & 0 & 0 & 0 \\ 0 & -S & 0 & 0 \\ 0 & 0 & -S & 0 \\ 0 & 0 & 0 & -1-S \end{vmatrix} = S^2(S+1)(S-1) = 0$$

$$\begin{vmatrix} \frac{A}{4}-T & 0 & 0 & 0 \\ 0 & -\frac{A}{4}-T & \frac{A}{2} & 0 \\ 0 & \frac{A}{2} & -\frac{A}{4}-T & 0 \\ 0 & 0 & 0 & \frac{A}{4}-T \end{vmatrix} = (T+\frac{3A}{4})(T-\frac{A}{4})^3 = 0$$

解得$R = 0$或$R = 2$（相应的，$a = 0$或$a = 1$），$S = 0$或$S = 1$或$S = -1$（相应的，$b = 0$或$b = 1$或$b = -1$），$T = \frac{A}{4}$或$T = -\frac{3A}{4}$，现在我们回代到原方程。当$R = 0$时，第一个矩阵等式变为：

$$\hbar^2 \begin{pmatrix} 2-R & 0 & 0 & 0 \\ 0 & 1-R & 1 & 0 \\ 0 & 1 & 1-R & 0 \\ 0 & 0 & 0 & 2-R \end{pmatrix} \begin{pmatrix} c_{\alpha\alpha} \\ c_{\alpha\beta} \\ c_{\beta\alpha} \\ c_{\beta\beta} \end{pmatrix} = 0 \Rightarrow \hbar^2 \begin{pmatrix} 2 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 2 \end{pmatrix} \begin{pmatrix} c_{\alpha\alpha} \\ c_{\alpha\beta} \\ c_{\beta\alpha} \\ c_{\beta\beta} \end{pmatrix} = 0 \Rightarrow \begin{cases} c_{\alpha\alpha} = c_{\beta\beta} = 0 \\ c_{\alpha\beta} + c_{\beta\alpha} = 0 \end{cases}$$

结合耦合表象态矢的归一性，可得$c_{\alpha\beta} = -c_{\beta\alpha} = \pm\frac{1}{\sqrt{2}}$，因此$R = 0\ (a = 0)$对应的态矢为

$|0b\rangle = \frac{1}{\sqrt{2}}(|\alpha\beta\rangle - |\beta\alpha\rangle)$，带回第二个、第三个矩阵等式，得：

$$\hbar \begin{pmatrix} 1-S & 0 & 0 & 0 \\ 0 & -S & 0 & 0 \\ 0 & 0 & -S & 0 \\ 0 & 0 & 0 & -1-S \end{pmatrix} \begin{pmatrix} c_{\alpha\alpha} \\ c_{\alpha\beta} \\ c_{\beta\alpha} \\ c_{\beta\beta} \end{pmatrix} = 0 \Rightarrow \hbar \begin{pmatrix} 1-S & 0 & 0 & 0 \\ 0 & -S & 0 & 0 \\ 0 & 0 & -S & 0 \\ 0 & 0 & 0 & -1-S \end{pmatrix} \begin{pmatrix} 0 \\ \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \\ 0 \end{pmatrix} = 0 \Rightarrow S = 0 \Rightarrow b = 0$$

$$\hbar^2 \begin{pmatrix} \frac{A}{4}-T & 0 & 0 & 0 \\ 0 & -\frac{A}{4}-T & \frac{A}{2} & 0 \\ 0 & \frac{A}{2} & -\frac{A}{4}-T & 0 \\ 0 & 0 & 0 & \frac{A}{4}-T \end{pmatrix} \begin{pmatrix} c_{\alpha\alpha} \\ c_{\alpha\beta} \\ c_{\beta\alpha} \\ c_{\beta\beta} \end{pmatrix} = 0 \Rightarrow \hbar^2 \begin{pmatrix} \frac{A}{4}-T & 0 & 0 & 0 \\ 0 & -\frac{A}{4}-T & \frac{A}{2} & 0 \\ 0 & \frac{A}{2} & -\frac{A}{4}-T & 0 \\ 0 & 0 & 0 & \frac{A}{4}-T \end{pmatrix} \begin{pmatrix} 0 \\ \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \\ 0 \end{pmatrix} = 0 \Rightarrow T = -\frac{3A}{4}$$

因此第一个耦合态矢为$|00\rangle = \frac{1}{\sqrt{2}}(|\alpha\beta\rangle - |\beta\alpha\rangle)$，满足$\hat{\boldsymbol{S}}^2|00\rangle = 0\cdot(0+1)\hbar^2|00\rangle = 0$，

$\hat{S}_z|00\rangle = 0\hbar|00\rangle = 0$，$\hat{H}|00\rangle = -\frac{3A}{4}\hbar^2|00\rangle$

当$R = 2$时，第一个矩阵等式变为：

$$\hbar^2 \begin{pmatrix} 2-R & 0 & 0 & 0 \\ 0 & 1-R & 1 & 0 \\ 0 & 1 & 1-R & 0 \\ 0 & 0 & 0 & 2-R \end{pmatrix} \begin{pmatrix} c_{\alpha\alpha} \\ c_{\alpha\beta} \\ c_{\beta\alpha} \\ c_{\beta\beta} \end{pmatrix} = 0 \Rightarrow \hbar^2 \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & -1 & 1 & 0 \\ 0 & 1 & -1 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} c_{\alpha\alpha} \\ c_{\alpha\beta} \\ c_{\beta\alpha} \\ c_{\beta\beta} \end{pmatrix} = 0 \Rightarrow c_{\alpha\beta} - c_{\beta\alpha} = 0$$

因此仅从第一个矩阵等式无法得出态矢，得从第二个矩阵等式下手。当$S = 1$时，第二个矩阵等式变为：

$$\hbar \begin{pmatrix} 1-S & 0 & 0 & 0 \\ 0 & -S & 0 & 0 \\ 0 & 0 & -S & 0 \\ 0 & 0 & 0 & -1-S \end{pmatrix} \begin{pmatrix} c_{\alpha\alpha} \\ c_{\alpha\beta} \\ c_{\beta\alpha} \\ c_{\beta\beta} \end{pmatrix} = 0 \Rightarrow \hbar \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -2 \end{pmatrix} \begin{pmatrix} c_{\alpha\alpha} \\ c_{\alpha\beta} \\ c_{\beta\alpha} \\ c_{\beta\beta} \end{pmatrix} = 0 \Rightarrow c_{\alpha\beta} = c_{\beta\alpha} = c_{\beta\beta} = 0$$

显然满足$c_{\alpha\beta} - c_{\beta\alpha} = 0$的条件，结合耦合表象态矢的归一性，得$c_{\alpha\alpha} = \pm 1$，因此$\begin{cases} R = 2 \\ S = 1 \end{cases}$（即

$\begin{cases} a = 1 \\ b = 1 \end{cases}$）时，对应态矢为$|11\rangle = |\alpha\alpha\rangle$，带回第三个矩阵等式，得：

$$\hbar^2 \begin{pmatrix} \frac{A}{4}-T & 0 & 0 & 0 \\ 0 & -\frac{A}{4}-T & \frac{A}{2} & 0 \\ 0 & \frac{A}{2} & -\frac{A}{4}-T & 0 \\ 0 & 0 & 0 & \frac{A}{4}-T \end{pmatrix} \begin{pmatrix} c_{\alpha\alpha} \\ c_{\alpha\beta} \\ c_{\beta\alpha} \\ c_{\beta\beta} \end{pmatrix} = 0 \Rightarrow \hbar^2 \begin{pmatrix} \frac{A}{4}-T & 0 & 0 & 0 \\ 0 & -\frac{A}{4}-T & \frac{A}{2} & 0 \\ 0 & \frac{A}{2} & -\frac{A}{4}-T & 0 \\ 0 & 0 & 0 & \frac{A}{4}-T \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix} = 0 \Rightarrow T = \frac{A}{4}$$

因此第二个耦合态矢为$|11\rangle = |\alpha\alpha\rangle$，满足$\hat{\boldsymbol{S}}^2|11\rangle = 1\cdot(1+1)\hbar^2|11\rangle = 2\hbar^2|11\rangle$，$\hat{S}_z|11\rangle = \hbar|11\rangle$，

$\hat{H}|11\rangle = \frac{A}{4}\hbar^2|11\rangle$

当$S = -1$时，第二个矩阵等式变为：

$$\hbar \begin{pmatrix} 1-S & 0 & 0 & 0 \\ 0 & -S & 0 & 0 \\ 0 & 0 & -S & 0 \\ 0 & 0 & 0 & -1-S \end{pmatrix} \begin{pmatrix} c_{\alpha\alpha} \\ c_{\alpha\beta} \\ c_{\beta\alpha} \\ c_{\beta\beta} \end{pmatrix} = 0 \Rightarrow \hbar \begin{pmatrix} 2 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} c_{\alpha\alpha} \\ c_{\alpha\beta} \\ c_{\beta\alpha} \\ c_{\beta\beta} \end{pmatrix} = 0 \Rightarrow c_{\alpha\alpha} = c_{\alpha\beta} = c_{\beta\alpha} = 0$$

显然也满足$c_{\alpha\beta} - c_{\beta\alpha} = 0$的条件，结合耦合表象态矢的归一性，得$c_{\beta\beta} = \pm 1$，因此$\begin{cases} R = 2 \\ S = -1 \end{cases}$（即

$\begin{cases} a = 1 \\ b = -1 \end{cases}$）时，对应态矢为$|1\bar{1}\rangle = |\beta\beta\rangle$，带回第三个矩阵等式，得：

$$\hbar^2 \begin{pmatrix} \frac{A}{4}-T & 0 & 0 & 0 \\ 0 & -\frac{A}{4}-T & \frac{A}{2} & 0 \\ 0 & \frac{A}{2} & -\frac{A}{4}-T & 0 \\ 0 & 0 & 0 & \frac{A}{4}-T \end{pmatrix} \begin{pmatrix} c_{\alpha\alpha} \\ c_{\alpha\beta} \\ c_{\beta\alpha} \\ c_{\beta\beta} \end{pmatrix} = 0 \Rightarrow \hbar^2 \begin{pmatrix} \frac{A}{4}-T & 0 & 0 & 0 \\ 0 & -\frac{A}{4}-T & \frac{A}{2} & 0 \\ 0 & \frac{A}{2} & -\frac{A}{4}-T & 0 \\ 0 & 0 & 0 & \frac{A}{4}-T \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix} = 0 \Rightarrow T = \frac{A}{4}$$

因此第三个耦合态矢为 $|1\bar{1}\rangle = |\beta\beta\rangle$，满足 $\hat{\boldsymbol{S}}^2|1\bar{1}\rangle = 1 \cdot (1+1)\hbar^2|1\bar{1}\rangle = 2\hbar^2|1\bar{1}\rangle$，$\hat{S}_z|1\bar{1}\rangle = -\hbar|1\bar{1}\rangle$，$\hat{H}|1\bar{1}\rangle = \frac{A}{4}\hbar^2|1\bar{1}\rangle$

当 $S=0$ 时，第二个矩阵等式变为：

$$\hbar \begin{pmatrix} 1-S & 0 & 0 & 0 \\ 0 & -S & 0 & 0 \\ 0 & 0 & -S & 0 \\ 0 & 0 & 0 & -1-S \end{pmatrix} \begin{pmatrix} c_{\alpha\alpha} \\ c_{\alpha\beta} \\ c_{\beta\alpha} \\ c_{\beta\beta} \end{pmatrix} = 0 \Rightarrow \hbar \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} c_{\alpha\alpha} \\ c_{\alpha\beta} \\ c_{\beta\alpha} \\ c_{\beta\beta} \end{pmatrix} = 0 \Rightarrow c_{\alpha\alpha} = c_{\beta\beta} = 0$$

若结合 $R=2$ 时推出的条件 $c_{\alpha\beta} - c_{\beta\alpha} = 0$，结合耦合表象态矢的归一性，可得 $c_{\alpha\beta} = c_{\beta\alpha} = \pm\frac{1}{\sqrt{2}}$，从而 $\begin{cases} R=2 \\ S=0 \end{cases}$（即 $\begin{cases} a=1 \\ b=0 \end{cases}$）时，对应态矢为 $|10\rangle = \frac{1}{\sqrt{2}}(|\alpha\beta\rangle + |\beta\alpha\rangle)$，带回第三个矩阵等式，得：

$$\hbar^2 \begin{pmatrix} \frac{A}{4}-T & 0 & 0 & 0 \\ 0 & -\frac{A}{4}-T & \frac{A}{2} & 0 \\ 0 & \frac{A}{2} & -\frac{A}{4}-T & 0 \\ 0 & 0 & 0 & \frac{A}{4}-T \end{pmatrix} \begin{pmatrix} c_{\alpha\alpha} \\ c_{\alpha\beta} \\ c_{\beta\alpha} \\ c_{\beta\beta} \end{pmatrix} = 0 \Rightarrow \hbar^2 \begin{pmatrix} \frac{A}{4}-T & 0 & 0 & 0 \\ 0 & -\frac{A}{4}-T & \frac{A}{2} & 0 \\ 0 & \frac{A}{2} & -\frac{A}{4}-T & 0 \\ 0 & 0 & 0 & \frac{A}{4}-T \end{pmatrix} \begin{pmatrix} 0 \\ \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \\ 0 \end{pmatrix} = 0 \Rightarrow T = \frac{A}{4}$$

因此第四个耦合态矢为 $|10\rangle = \frac{1}{\sqrt{2}}(|\alpha\beta\rangle + |\beta\alpha\rangle)$，满足 $\hat{\boldsymbol{S}}^2|10\rangle = 1 \cdot (1+1)\hbar^2|10\rangle = 2\hbar^2|10\rangle$，$\hat{S}_z|10\rangle = 0\hbar|10\rangle = 0$，$\hat{H}|10\rangle = \frac{A}{4}\hbar^2|10\rangle$

最后我们总结一下每一个能级的简并度和耦合态矢关于两个电子交换的对称性。观察这四个耦合态矢可知，能量为 $E = -\frac{3A}{4}$ 的态为 $|00\rangle$，它是自旋单重态，简并度为1；能量为 $E = \frac{A}{4}$ 的态为 $|11\rangle, |10\rangle, |1\bar{1}\rangle$，它是自旋三重态，简并度为3。此外，设交换电子的操作可以用算符 $\hat{P}$ 表示，则有 $\hat{P}|00\rangle = \frac{1}{\sqrt{2}}(|\beta\alpha\rangle - |\alpha\beta\rangle) = -|00\rangle$，$\hat{P}|11\rangle = |\alpha\alpha\rangle = |11\rangle$，$\hat{P}|10\rangle = \frac{1}{\sqrt{2}}(|\beta\alpha\rangle + |\alpha\beta\rangle) = |10\rangle$，$\hat{P}|1\bar{1}\rangle = |\beta\beta\rangle = |1\bar{1}\rangle$，因此 $|00\rangle$ 关于两个电子交换是反对称的，$|11\rangle, |10\rangle, |1\bar{1}\rangle$ 关于两个电子交换是对称的

4.4 计算旋转算符在 $j=1$ 的角动量本征态上的表示矩阵，并与4.5.8比较，它们的同异在哪里？

解：对于 $j=1$ 的角动量本征态，有 $m = 0, \pm1$，而 $\hat{J}_y = \frac{1}{2i}(\hat{J}_+ - \hat{J}_-)$，因此有：

$$\hat{J}_y|j=1,m\rangle = \frac{1}{2i}(\hat{J}_+ - \hat{J}_-)|j=1,m\rangle = \frac{1}{2i}\hat{J}_+|j=1,m\rangle - \frac{1}{2i}\hat{J}_-|j=1,m\rangle$$
$$= \frac{1}{2i}\sqrt{1(1+1) - m(m+1)}\hbar|j=1,m+1\rangle - \frac{1}{2i}\sqrt{1(1+1) - m(m-1)}\hbar|j=1,m-1\rangle$$
$$= \frac{\sqrt{-(m-1)(m+2)}\hbar}{2i}|j=1,m+1\rangle - \frac{\sqrt{-(m-2)(m+1)}\hbar}{2i}|j=1,m-1\rangle$$

从而得 $\hat{J}_y$ 对应的矩阵形式为 $\boldsymbol{J}_y = \frac{\sqrt{2}i\hbar}{2}\begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix}$，因此 $-\frac{i}{\hbar}\boldsymbol{J}_y\theta = \frac{\sqrt{2}\theta}{2}\begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix}$，

$$e^{-\frac{i}{\hbar}\boldsymbol{J}_y\theta} = 1 + \sum_{k=1}^{\infty} \frac{1}{k!}\left(\frac{\sqrt{2}\theta}{2}\right)^k \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix}^k$$ 。现在我们要考察矩阵的幂，显然：

$$< Empty\ Math\ Block >$$

4.5 对于轨道角动量算符 $\hat{\boldsymbol{L}}$，证明 $\hat{\boldsymbol{L}}^2 = \hat{\boldsymbol{r}}^2\hat{\boldsymbol{p}}^2 - (\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}})^2 + \mathrm{i}\hbar\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}}$

证明：由于 $\hat{\boldsymbol{L}} = \hat{\boldsymbol{r}}\times\hat{\boldsymbol{p}} = \begin{vmatrix} \boldsymbol{i} & \boldsymbol{j} & \boldsymbol{k} \\ \hat{r}_x & \hat{r}_y & \hat{r}_z \\ \hat{p}_x & \hat{p}_y & \hat{p}_z \end{vmatrix}$，而 $\hat{\boldsymbol{r}}^2 = \hat{r}_x^2 + \hat{r}_y^2 + \hat{r}_z^2$，$\hat{\boldsymbol{p}}^2 = \hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2$，

$\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}} = \hat{r}_x\hat{p}_x + \hat{r}_y\hat{p}_y + \hat{r}_z\hat{p}_z$，因此有：

$$
\begin{aligned}
\hat{\boldsymbol{L}}^2 &= (\hat{\boldsymbol{r}}\times\hat{\boldsymbol{p}})^2 = [(\hat{r}_y\hat{p}_z - \hat{r}_z\hat{p}_y)\boldsymbol{i} + (\hat{r}_z\hat{p}_x - \hat{r}_x\hat{p}_z)\boldsymbol{j} + (\hat{r}_x\hat{p}_y - \hat{r}_y\hat{p}_x)\boldsymbol{k}]^2 \\
&= (\hat{r}_y\hat{p}_z - \hat{r}_z\hat{p}_y)^2 + (\hat{r}_z\hat{p}_x - \hat{r}_x\hat{p}_z)^2 + (\hat{r}_x\hat{p}_y - \hat{r}_y\hat{p}_x)^2 \\
&= (\hat{r}_y\hat{p}_z\hat{r}_y\hat{p}_z - \hat{r}_y\hat{p}_z\hat{r}_z\hat{p}_y - \hat{r}_z\hat{p}_y\hat{r}_y\hat{p}_z + \hat{r}_z\hat{p}_y\hat{r}_z\hat{p}_y) \\
&\quad + (\hat{r}_z\hat{p}_x\hat{r}_z\hat{p}_x - \hat{r}_z\hat{p}_x\hat{r}_x\hat{p}_z - \hat{r}_x\hat{p}_z\hat{r}_z\hat{p}_x + \hat{r}_x\hat{p}_z\hat{r}_x\hat{p}_z) \\
&\quad + (\hat{r}_x\hat{p}_y\hat{r}_x\hat{p}_y - \hat{r}_x\hat{p}_y\hat{r}_y\hat{p}_x - \hat{r}_y\hat{p}_x\hat{r}_x\hat{p}_y + \hat{r}_y\hat{p}_x\hat{r}_y\hat{p}_x) \\
&= [\hat{r}_y\hat{r}_y\hat{p}_z\hat{p}_z + \hat{r}_y([\hat{r}_z,\hat{p}_z] - \hat{r}_z\hat{p}_z)\hat{p}_y + \hat{r}_z([\hat{r}_y,\hat{p}_y] - \hat{r}_y\hat{p}_y)\hat{p}_z + \hat{r}_z\hat{r}_z\hat{p}_y\hat{p}_y] \\
&\quad + [\hat{r}_z\hat{r}_z\hat{p}_x\hat{p}_x + \hat{r}_z([\hat{r}_x,\hat{p}_x] - \hat{r}_x\hat{p}_x)\hat{p}_z + \hat{r}_x([\hat{r}_z,\hat{p}_z] - \hat{r}_z\hat{p}_z)\hat{p}_x + \hat{r}_x\hat{r}_x\hat{p}_z\hat{p}_z] \\
&\quad + [\hat{r}_x\hat{r}_x\hat{p}_y\hat{p}_y + \hat{r}_x([\hat{r}_y,\hat{p}_y] - \hat{r}_y\hat{p}_y)\hat{p}_x + \hat{r}_y([\hat{r}_x,\hat{p}_x] - \hat{r}_x\hat{p}_x)\hat{p}_y + \hat{r}_y\hat{r}_y\hat{p}_x\hat{p}_x] \\
&= [\hat{r}_y^2\hat{p}_z^2 + \hat{r}_y(\mathrm{i}\hbar - \hat{r}_z\hat{p}_z)\hat{p}_y + \hat{r}_z(\mathrm{i}\hbar - \hat{r}_y\hat{p}_y)\hat{p}_z + \hat{r}_z^2\hat{p}_y^2] \\
&\quad + [\hat{r}_z^2\hat{p}_x^2 + \hat{r}_z(\mathrm{i}\hbar - \hat{r}_x\hat{p}_x)\hat{p}_z + \hat{r}_x(\mathrm{i}\hbar - \hat{r}_z\hat{p}_z)\hat{p}_x + \hat{r}_x^2\hat{p}_z^2] \\
&\quad + [\hat{r}_x^2\hat{p}_y^2 + \hat{r}_x(\mathrm{i}\hbar - \hat{r}_y\hat{p}_y)\hat{p}_x + \hat{r}_y(\mathrm{i}\hbar - \hat{r}_x\hat{p}_x)\hat{p}_y + \hat{r}_y^2\hat{p}_x^2] \\
&= [\hat{r}_y^2\hat{p}_z^2 - \hat{r}_y\hat{r}_z\hat{p}_z\hat{p}_y - \hat{r}_z\hat{r}_y\hat{p}_y\hat{p}_z + \hat{r}_z^2\hat{p}_y^2] + [\hat{r}_z^2\hat{p}_x^2 - \hat{r}_z\hat{r}_x\hat{p}_x\hat{p}_z - \hat{r}_x\hat{r}_z\hat{p}_z\hat{p}_x + \hat{r}_x^2\hat{p}_z^2] \\
&\quad + [\hat{r}_x^2\hat{p}_y^2 - \hat{r}_x\hat{r}_y\hat{p}_y\hat{p}_x - \hat{r}_y\hat{r}_x\hat{p}_x\hat{p}_y + \hat{r}_y^2\hat{p}_x^2] + 2\mathrm{i}\hbar(\hat{r}_x\hat{p}_x + \hat{r}_y\hat{p}_y + \hat{r}_z\hat{p}_z) \\
&= (\hat{r}_x^2 + \hat{r}_y^2 + \hat{r}_z^2)(\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2) + 2\mathrm{i}\hbar(\hat{r}_x\hat{p}_x + \hat{r}_y\hat{p}_y + \hat{r}_z\hat{p}_z) - (\hat{r}_x^2\hat{p}_x^2 + \hat{r}_y^2\hat{p}_y^2 + \hat{r}_z^2\hat{p}_z^2) \\
&\quad - (\hat{r}_y\hat{r}_z\hat{p}_z\hat{p}_y + \hat{r}_z\hat{r}_y\hat{p}_y\hat{p}_z + \hat{r}_z\hat{r}_x\hat{p}_x\hat{p}_z + \hat{r}_x\hat{r}_z\hat{p}_z\hat{p}_x + \hat{r}_x\hat{r}_y\hat{p}_y\hat{p}_x + \hat{r}_y\hat{r}_x\hat{p}_x\hat{p}_y) \\
&= \hat{\boldsymbol{r}}^2\hat{\boldsymbol{p}}^2 + 2\mathrm{i}\hbar\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}} - [\hat{r}_x([\hat{r}_x,\hat{p}_x] + \hat{p}_x\hat{r}_x)\hat{p}_x + \hat{r}_y([\hat{r}_y,\hat{p}_y] + \hat{p}_y\hat{r}_y)\hat{p}_y + \hat{r}_z([\hat{r}_z,\hat{p}_z] + \hat{p}_z\hat{r}_z)\hat{p}_z] \\
&\quad - (\hat{r}_y\hat{r}_z\hat{p}_z\hat{p}_y + \hat{r}_z\hat{r}_y\hat{p}_y\hat{p}_z + \hat{r}_z\hat{r}_x\hat{p}_x\hat{p}_z + \hat{r}_x\hat{r}_z\hat{p}_z\hat{p}_x + \hat{r}_x\hat{r}_y\hat{p}_y\hat{p}_x + \hat{r}_y\hat{r}_x\hat{p}_x\hat{p}_y) \\
&= \hat{\boldsymbol{r}}^2\hat{\boldsymbol{p}}^2 + 2\mathrm{i}\hbar\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}} - \mathrm{i}\hbar(\hat{r}_x\hat{p}_x + \hat{r}_y\hat{p}_y + \hat{r}_z\hat{p}_z) - (\hat{r}_x\hat{p}_x + \hat{r}_y\hat{p}_y + \hat{r}_z\hat{p}_z)^2 \\
&= \hat{\boldsymbol{r}}^2\hat{\boldsymbol{p}}^2 - (\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}})^2 + \mathrm{i}\hbar\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}}
\end{aligned}
$$

故原题得证

另证：由于 $\hat{\boldsymbol{L}} = \hat{\boldsymbol{r}}\times\hat{\boldsymbol{p}}$，因此利用混合积的轮换性 $\begin{cases} \hat{a}\cdot(\hat{b}\times\hat{c}) = \hat{b}\cdot(\hat{c}\times\hat{a}) = \hat{c}\cdot(\hat{a}\times\hat{b}) \\ (\hat{b}\times\hat{c})\cdot\hat{a} = (\hat{c}\times\hat{a})\cdot\hat{b} = (\hat{a}\times\hat{b})\cdot\hat{c} \end{cases}$，以及外积的反交换性 $\hat{a}\times\hat{b} = -\hat{b}\times\hat{a}$，得：

$$
\begin{aligned}
\hat{\boldsymbol{L}}^2 &= (\hat{\boldsymbol{r}}\times\hat{\boldsymbol{p}})^2 = (\hat{\boldsymbol{r}}\times\hat{\boldsymbol{p}})\cdot(\hat{\boldsymbol{r}}\times\hat{\boldsymbol{p}}) = -(\hat{\boldsymbol{r}}\times\hat{\boldsymbol{p}})\cdot(\hat{\boldsymbol{p}}\times\hat{\boldsymbol{r}}) = -[(\hat{\boldsymbol{p}}\times\hat{\boldsymbol{r}})\times\hat{\boldsymbol{r}}]\cdot\hat{\boldsymbol{p}} = -[(\hat{\boldsymbol{p}}\cdot\hat{\boldsymbol{r}})\hat{\boldsymbol{r}} - \hat{\boldsymbol{p}}(\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{r}})]\cdot\hat{\boldsymbol{p}} \\
&= -(\hat{\boldsymbol{p}}\cdot\hat{\boldsymbol{r}})(\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}}) + (\hat{\boldsymbol{p}}\hat{\boldsymbol{r}}^2)\cdot\hat{\boldsymbol{p}} = -(\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}} - \mathrm{i}\hbar\nabla\cdot\hat{\boldsymbol{r}})(\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}}) + (\hat{\boldsymbol{r}}^2\hat{\boldsymbol{p}} - \mathrm{i}\hbar\nabla\hat{\boldsymbol{r}}^2)\cdot\hat{\boldsymbol{p}} \\
&= -(\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}} - 3\mathrm{i}\hbar)(\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}}) + (\hat{\boldsymbol{r}}^2\hat{\boldsymbol{p}} - 2\mathrm{i}\hbar\hat{\boldsymbol{r}})\cdot\hat{\boldsymbol{p}} = -(\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}})^2 + 3\mathrm{i}\hbar\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}} + \hat{\boldsymbol{r}}^2\hat{\boldsymbol{p}}^2 - 2\mathrm{i}\hbar\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}} \\
&= \hat{\boldsymbol{r}}^2\hat{\boldsymbol{p}}^2 - (\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}})^2 + \mathrm{i}\hbar\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}}
\end{aligned}
$$

4.6 考虑对应于 d 轨道的轨道角动量本征态与电子自旋本征态之间的耦合，写出用未耦合表象的基矢

$$|ls; mm_s\rangle \equiv |lm\rangle \otimes |sm_s\rangle \quad (l = 2; m = 0, \pm1, \pm2; s = \frac{1}{2}; m_s = \pm\frac{1}{2})$$

所表示的耦合表象本征态 $|jm; ls\rangle$ 表达式

解：首先我们知道 $|l - s| \le j \le l + s$，代入得 $\frac{3}{2} \le j \le \frac{5}{2}$（实际上 j 只能取 $\frac{5}{2}$ 或 $\frac{3}{2}$）。其次，$-\frac{5}{2} = -2 - \frac{1}{2} \le m + m_s \le 2 + \frac{1}{2} = \frac{5}{2}$，即 $-(l + s) \le m + m_s \le l + s$。对于不等式取等号的情形，我们有（以下对耦合表象，只写出 j 和 m_c，其中 m_c 为耦合后 $\hat{J}_z$ 的本征值，满足 $m_c = m + m_s$；对未耦合表象，只写出 m_1 和 m_2）：

$$\left|j = \frac{5}{2}, m_c = \frac{5}{2}\right\rangle = \left|m = 2, m_s = \frac{1}{2}\right\rangle \quad \left|j = \frac{5}{2}, m_c = -\frac{5}{2}\right\rangle = \left|m = -2, m_s = -\frac{1}{2}\right\rangle$$

对第一个式子两边使用总降算符$\hat{J}_-$，得:

$$\hat{J}_-|j=\frac{5}{2},m_c=\frac{5}{2}\rangle = \sqrt{\frac{5}{2}(\frac{5}{2}+1)-\frac{5}{2}(\frac{5}{2}-1)}\hbar|j=\frac{5}{2},m_c=\frac{3}{2}\rangle = \sqrt{5}\hbar|j=\frac{5}{2},m_c=\frac{3}{2}\rangle$$

$$\hat{J}_-|m=2,m_s=\frac{1}{2}\rangle = (\hat{L}_-+\hat{S}_-)|m=2,m_s=\frac{1}{2}\rangle = \hat{L}_-|m=2,m_s=\frac{1}{2}\rangle + \hat{S}_-|m=2,m_s=\frac{1}{2}\rangle$$
$$= \sqrt{2(2+1)-2(2-1)}\hbar|m=1,m_s=\frac{1}{2}\rangle + \sqrt{\frac{1}{2}(\frac{1}{2}+1)-\frac{1}{2}(\frac{1}{2}-1)}\hbar|m=2,m_s=-\frac{1}{2}\rangle$$
$$= 2\hbar|m=1,m_s=\frac{1}{2}\rangle + \hbar|m=2,m_s=-\frac{1}{2}\rangle$$

从而有$|j=\frac{5}{2},m_c=\frac{3}{2}\rangle = \sqrt{\frac{4}{5}}|m=1,m_s=\frac{1}{2}\rangle + \sqrt{\frac{1}{5}}|m=2,m_s=-\frac{1}{2}\rangle$，对两边再次使用总降算符$\hat{J}_-$，得:

$$\hat{J}_-|j=\frac{5}{2},m_c=\frac{3}{2}\rangle = \sqrt{\frac{5}{2}(\frac{5}{2}+1)-\frac{3}{2}(\frac{3}{2}-1)}\hbar|j=\frac{5}{2},m_c=\frac{1}{2}\rangle = 2\sqrt{2}\hbar|j=\frac{5}{2},m_c=\frac{1}{2}\rangle$$

$$\hat{J}_-|m=1,m_s=\frac{1}{2}\rangle = (\hat{L}_-+\hat{S}_-)|m=1,m_s=\frac{1}{2}\rangle = \hat{L}_-|m=1,m_s=\frac{1}{2}\rangle + \hat{S}_-|m=1,m_s=\frac{1}{2}\rangle$$
$$= \sqrt{2(2+1)-1(1-1)}\hbar|m=0,m_s=\frac{1}{2}\rangle + \sqrt{\frac{1}{2}(\frac{1}{2}+1)-\frac{1}{2}(\frac{1}{2}-1)}\hbar|m=1,m_s=-\frac{1}{2}\rangle$$
$$= \sqrt{6}\hbar|m=0,m_s=\frac{1}{2}\rangle + \hbar|m=1,m_s=-\frac{1}{2}\rangle$$

$$\hat{J}_-|m=2,m_s=-\frac{1}{2}\rangle = (\hat{L}_-+\hat{S}_-)|m=2,m_s=-\frac{1}{2}\rangle = \hat{L}_-|m=2,m_s=-\frac{1}{2}\rangle + \hat{S}_-|m=2,m_s=-\frac{1}{2}\rangle$$
$$= \sqrt{2(2+1)-2(1-1)}\hbar|m=1,m_s=-\frac{1}{2}\rangle + 0 = 2\hbar|m=1,m_s=-\frac{1}{2}\rangle$$

$$\hat{J}_-(\sqrt{\frac{4}{5}}|m=1,m_s=\frac{1}{2}\rangle + \sqrt{\frac{1}{5}}|m=2,m_s=-\frac{1}{2}\rangle) = \sqrt{\frac{4}{5}}\hat{J}_-|m=1,m_s=\frac{1}{2}\rangle + \sqrt{\frac{1}{5}}\hat{J}_-|m=2,m_s=-\frac{1}{2}\rangle$$
$$= \sqrt{\frac{4}{5}}(\sqrt{6}\hbar|m=0,m_s=\frac{1}{2}\rangle + \hbar|m=1,m_s=-\frac{1}{2}\rangle) + \sqrt{\frac{1}{5}}(2\hbar|m=1,m_s=-\frac{1}{2}\rangle)$$
$$= \sqrt{\frac{24}{5}}\hbar|m=0,m_s=\frac{1}{2}\rangle + \sqrt{\frac{16}{5}}|m=1,m_s=-\frac{1}{2}\rangle$$

从而有$|j=\frac{5}{2},m_c=\frac{1}{2}\rangle = \sqrt{\frac{3}{5}}\hbar|m=0,m_s=\frac{1}{2}\rangle + \sqrt{\frac{2}{5}}|m=1,m_s=-\frac{1}{2}\rangle$

对第二个式子两边使用总升算符$\hat{J}_+$，得:

$$\hat{J}_+|j=\frac{5}{2},m_c=-\frac{5}{2}\rangle = \sqrt{\frac{5}{2}(\frac{5}{2}+1)-(-\frac{5}{2})(-\frac{5}{2}+1)}\hbar|j=\frac{5}{2},m_c=-\frac{3}{2}\rangle = \sqrt{5}\hbar|j=\frac{5}{2},m_c=-\frac{3}{2}\rangle$$

$$\hat{J}_+|m=-2,m_s=-\frac{1}{2}\rangle = (\hat{L}_++\hat{S}_+)|m=-2,m_s=-\frac{1}{2}\rangle = \hat{L}_+|m=-2,m_s=-\frac{1}{2}\rangle + \hat{S}_+|m=-2,m_s=-\frac{1}{2}\rangle$$
$$= \sqrt{2(2+1)-(-2)(-2+1)}\hbar|m=-1,m_s=-\frac{1}{2}\rangle + \sqrt{\frac{1}{2}(\frac{1}{2}+1)-(-\frac{1}{2})(-\frac{1}{2}+1)}\hbar|m=-2,m_s=\frac{1}{2}\rangle$$
$$= 2\hbar|m=-1,m_s=-\frac{1}{2}\rangle + \hbar|m=-2,m_s=\frac{1}{2}\rangle$$

从而有$|j=\frac{5}{2},m_c=-\frac{3}{2}\rangle = \sqrt{\frac{4}{5}}|m=-1,m_s=-\frac{1}{2}\rangle + \sqrt{\frac{1}{5}}|m=-2,m_s=\frac{1}{2}\rangle$，对两边再次使用总升算符$\hat{J}_+$，得:

$$\hat{J}_+|j=\frac{5}{2},m_c=-\frac{3}{2}\rangle = \sqrt{\frac{5}{2}(\frac{5}{2}+1)-(-\frac{3}{2})(-\frac{3}{2}+1)}\hbar|j=\frac{5}{2},m_c=-\frac{1}{2}\rangle = 2\sqrt{2}\hbar|j=\frac{5}{2},m_c=-\frac{1}{2}\rangle$$

$$\hat{J}_+|m=-1,m_s=-\frac{1}{2}\rangle = (\hat{L}_+ + \hat{S}_+)|m=-1,m_s=-\frac{1}{2}\rangle = \hat{L}_+|m=-1,m_s=-\frac{1}{2}\rangle + \hat{S}_+|m=-1,m_s=-\frac{1}{2}\rangle$$

$$= \sqrt{2(2+1)-(-1)(-1+1)}\hbar|m=0,m_s=-\frac{1}{2}\rangle + \sqrt{\frac{1}{2}(\frac{1}{2}+1)-(-\frac{1}{2})(-\frac{1}{2}+1)}\hbar|m=-1,m_s=\frac{1}{2}\rangle$$

$$= \sqrt{6}\hbar|m=0,m_s=-\frac{1}{2}\rangle + \hbar|m=-1,m_s=\frac{1}{2}\rangle$$

$$\hat{J}_+|m=-2,m_s=\frac{1}{2}\rangle = (\hat{L}_+ + \hat{S}_+)|m=-2,m_s=\frac{1}{2}\rangle = \hat{L}_+|m=-2,m_s=\frac{1}{2}\rangle + \hat{S}_+|m=-2,m_s=\frac{1}{2}\rangle$$

$$= \sqrt{2(2+1)-(-2)(-2+1)}\hbar|m=-1,m_s=\frac{1}{2}\rangle + 0 = 2\hbar|m=-1,m_s=\frac{1}{2}\rangle$$

$$\hat{J}_+(\sqrt{\frac{4}{5}}|m=-1,m_s=-\frac{1}{2}\rangle + \sqrt{\frac{1}{5}}|m=-2,m_s=\frac{1}{2}\rangle) = \sqrt{\frac{4}{5}}\hat{J}_+|m=-1,m_s=-\frac{1}{2}\rangle + \sqrt{\frac{1}{5}}\hat{J}_+|m=-2,m_s=\frac{1}{2}\rangle$$

$$= \sqrt{\frac{4}{5}}(\sqrt{6}\hbar|m=0,m_s=-\frac{1}{2}\rangle + \hbar|m=-1,m_s=\frac{1}{2}\rangle) + \sqrt{\frac{1}{5}}(2\hbar|m=-1,m_s=\frac{1}{2}\rangle)$$

$$= \sqrt{\frac{24}{5}}\hbar|m=0,m_s=-\frac{1}{2}\rangle + \sqrt{\frac{16}{5}}\hbar|m=-1,m_s=\frac{1}{2}\rangle$$

从而有$|j=\frac{5}{2},m_c=-\frac{1}{2}\rangle = \sqrt{\frac{3}{5}}\hbar|m=0,m_s=-\frac{1}{2}\rangle + \sqrt{\frac{2}{5}}|m=-1,m_s=\frac{1}{2}\rangle$

接下来讨论$j=\frac{3}{2}$的情形，此时$m=\pm\frac{3}{2},\pm\frac{1}{2}$，因此设

$$\begin{cases} |j=\frac{3}{2},m_c=\frac{3}{2}\rangle = c_1|m=1,m_s=\frac{1}{2}\rangle + c_2|m=2,m_s=-\frac{1}{2}\rangle \\ |j=\frac{3}{2},m_c=\frac{1}{2}\rangle = c_3|m=0,m_s=\frac{1}{2}\rangle + c_4|m=1,m_s=-\frac{1}{2}\rangle \\ |j=\frac{3}{2},m_c=-\frac{1}{2}\rangle = c_5|m=0,m_s=-\frac{1}{2}\rangle + c_6|m=-1,m_s=\frac{1}{2}\rangle \\ |j=\frac{3}{2},m_c=-\frac{3}{2}\rangle = c_7|m=-1,m_s=-\frac{1}{2}\rangle + c_8|m=-2,m_s=\frac{1}{2}\rangle \end{cases}$$

其中$c_{1,3,5,7} \in \mathbb{R}^+$，$c_{2,4,6,8} \in \mathbb{R}$，则有:

$$\begin{cases} \langle j=\frac{3}{2},m_c=\frac{3}{2}|j=\frac{3}{2},m_c=\frac{3}{2}\rangle = c_1^2 + c_2^2 = 1 \\ \langle j=\frac{5}{2},m_c=\frac{3}{2}|j=\frac{3}{2},m_c=\frac{3}{2}\rangle = \sqrt{\frac{4}{5}}c_1 + \sqrt{\frac{1}{5}}c_2 = 0 \\ \langle j=\frac{3}{2},m_c=\frac{1}{2}|j=\frac{3}{2},m_c=\frac{1}{2}\rangle = c_3^2 + c_4^2 = 1 \\ \langle j=\frac{5}{2},m_c=\frac{1}{2}|j=\frac{3}{2},m_c=\frac{1}{2}\rangle = \sqrt{\frac{3}{5}}c_3 + \sqrt{\frac{2}{5}}c_4 = 0 \\ \langle j=\frac{3}{2},m_c=\frac{1}{2}|j=\frac{3}{2},m_c=-\frac{1}{2}\rangle = c_5^2 + c_6^2 = 1 \\ \langle j=\frac{5}{2},m_c=-\frac{1}{2}|j=\frac{3}{2},m_c=-\frac{1}{2}\rangle = \sqrt{\frac{3}{5}}c_5 + \sqrt{\frac{2}{5}}c_6 = 0 \\ \langle j=\frac{3}{2},m_c=-\frac{3}{2}|j=\frac{3}{2},m_c=-\frac{3}{2}\rangle = c_7^2 + c_8^2 = 1 \\ \langle j=\frac{5}{2},m_c=-\frac{3}{2}|j=\frac{3}{2},m_c=-\frac{3}{2}\rangle = \sqrt{\frac{4}{5}}c_7 + \sqrt{\frac{1}{5}}c_8 = 0 \end{cases}$$

解得

$$\begin{cases} c_1 = \sqrt{\frac{1}{5}}, c_2 = -\sqrt{\frac{4}{5}} \\ c_3 = \sqrt{\frac{2}{5}}, c_4 = -\sqrt{\frac{3}{5}} \\ c_5 = \sqrt{\frac{2}{5}}, c_6 = -\sqrt{\frac{3}{5}} \\ c_7 = \sqrt{\frac{1}{5}}, c_8 = -\sqrt{\frac{4}{5}} \end{cases}$$

因此有

$$\begin{cases} |j = \tfrac{3}{2}, m_c = \tfrac{3}{2}\rangle = \sqrt{\tfrac{1}{5}}|m = 1, m_s = \tfrac{1}{2}\rangle - \sqrt{\tfrac{4}{5}}|m = 2, m_s = -\tfrac{1}{2}\rangle \\[2mm] |j = \tfrac{3}{2}, m_c = \tfrac{1}{2}\rangle = \sqrt{\tfrac{2}{5}}|m = 0, m_s = \tfrac{1}{2}\rangle - \sqrt{\tfrac{3}{5}}|m = 1, m_s = -\tfrac{1}{2}\rangle \\[2mm] |j = \tfrac{3}{2}, m_c = -\tfrac{1}{2}\rangle = \sqrt{\tfrac{2}{5}}|m = 0, m_s = -\tfrac{1}{2}\rangle - \sqrt{\tfrac{3}{5}}|m = -1, m_s = \tfrac{1}{2}\rangle \\[2mm] |j = \tfrac{3}{2}, m_c = -\tfrac{3}{2}\rangle = \sqrt{\tfrac{1}{5}}|m = -1, m_s = -\tfrac{1}{2}\rangle - \sqrt{\tfrac{4}{5}}|m = -2, m_s = \tfrac{1}{2}\rangle \end{cases}$$