课堂练习

练习1：证明旋轨耦合中 $|j=\frac{1}{2},m=-\frac{1}{2}\rangle=\sqrt{\frac{1}{3}}|m_1=0,m_2=-\frac{1}{2}\rangle-\sqrt{\frac{2}{3}}|m_1=-1,m_2=\frac{1}{2}\rangle$

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

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

作矩阵乘法得：

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

两项相减，并忽略三次及更高次项，得：

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

又

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

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$\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}\boldsymbol{S}_y\theta}=\begin{pmatrix}\cos\frac{\theta}{2}&-\sin\frac{\theta}{2}\\\sin\frac{\theta}{2}&\cos\frac{\theta}{2}\end{pmatrix}$？

解：**（方法的提出）**我们可以采用如下方法推导$f(\hat{A})=\sum\limits_{i=0}^{\infty}\frac{f^{(i)}(0)}{i!}\hat{A}^i$的另一种表达形式，设算符$\hat{A}$的本征态矢为$|a_1\rangle,|a_2\rangle,\ldots$，相应的本征值为$a_1,a_2,\ldots$，则根据态矢的完备性，我们有

$$f(\hat{A})=\sum_{i=0}^{\infty}\frac{f^{(i)}(0)}{i!}\hat{A}^i=\sum_{i=0}^{\infty}\frac{f^{(i)}(0)}{i!}\hat{A}^i\sum_k|a_k\rangle\langle a_k|=\sum_k\sum_{i=0}^{\infty}\frac{f^{(i)}(0)}{i!}\hat{A}^i|a_k\rangle\langle a_k|=\sum_k\sum_{i=0}^{\infty}\frac{f^{(i)}(0)}{i!}a_k^i|a_k\rangle\langle a_k|=\sum_k f(a_k)|a_k\rangle\langle a_k|$$

从而$f(\hat{A})$在本征态矢上的矩阵表示为$f(\boldsymbol{A})=\mathrm{diag}(f(a_1),f(a_2),\ldots)$，而在另一态矢$|b_1\rangle,|b_2\rangle,\ldots$上的矩阵表示为

$$f(\tilde{\boldsymbol{A}})=\begin{pmatrix}\langle b_1|f(\hat{A})|b_1\rangle & \langle b_1|f(\hat{A})|b_2\rangle & \cdots\\ \langle b_2|f(\hat{A})|b_1\rangle & \langle b_2|f(\hat{A})|b_2\rangle & \cdots\\ \vdots & \vdots & \ddots\end{pmatrix}=\begin{pmatrix}\sum\limits_k f(a_k)\langle b_1|a_k\rangle\langle a_k|b_1\rangle & \sum\limits_k f(a_k)\langle b_1|a_k\rangle\langle a_k|b_2\rangle & \cdots\\ \sum\limits_k f(a_k)\langle b_2|a_k\rangle\langle a_k|b_1\rangle & \sum\limits_k f(a_k)\langle b_2|a_k\rangle\langle a_k|b_2\rangle & \cdots\\ \vdots & \vdots & \ddots\end{pmatrix}$$

另一方面，算符$\hat{A}$在本征态矢的矩阵表示为$\boldsymbol{A}=\mathrm{diag}(a_1,a_2,\ldots)$，而在另一态矢的矩阵表示为

$$\begin{aligned}\tilde{\boldsymbol{A}}&=\begin{pmatrix}\langle b_1|\hat{A}|b_1\rangle & \langle b_1|\hat{A}|b_2\rangle & \cdots\\ \langle b_2|\hat{A}|b_1\rangle & \langle b_2|\hat{A}|b_2\rangle & \cdots\\ \vdots & \vdots & \ddots\end{pmatrix}=\begin{pmatrix}\sum\limits_{i,j}\langle b_1|a_i\rangle\langle a_i|\hat{A}|a_j\rangle\langle a_j|b_1\rangle & \sum\limits_{i,j}\langle b_1|a_i\rangle\langle a_i|\hat{A}|a_j\rangle\langle a_j|b_2\rangle & \cdots\\ \sum\limits_{i,j}\langle b_2|a_i\rangle\langle a_i|\hat{A}|a_j\rangle\langle a_j|b_1\rangle & \sum\limits_{i,j}\langle b_2|a_i\rangle\langle a_i|\hat{A}|a_j\rangle\langle a_j|b_2\rangle & \cdots\\ \vdots & \vdots & \ddots\end{pmatrix}\\
&=\begin{pmatrix}\sum\limits_k a_k\langle b_1|a_k\rangle\langle a_k|b_1\rangle & \sum\limits_k a_k\langle b_1|a_k\rangle\langle a_k|b_2\rangle & \cdots\\ \sum\limits_k a_k\langle b_2|a_k\rangle\langle a_k|b_1\rangle & \sum\limits_k a_k\langle b_2|a_k\rangle\langle a_k|b_2\rangle & \cdots\\ \vdots & \vdots & \ddots\end{pmatrix}=\begin{pmatrix}a_1\langle b_1|a_1\rangle & a_2\langle b_1|a_2\rangle & \cdots\\ a_1\langle b_2|a_1\rangle & a_2\langle b_2|a_2\rangle & \cdots\\ \vdots & \vdots & \ddots\end{pmatrix}\begin{pmatrix}\langle a_1|b_1\rangle & \langle a_1|b_2\rangle & \cdots\\ \langle a_2|b_1\rangle & \langle a_2|b_2\rangle & \cdots\\ \vdots & \vdots & \ddots\end{pmatrix}\\
&=\begin{pmatrix}\langle b_1|a_1\rangle & \langle b_1|a_2\rangle & \cdots\\ \langle b_2|a_1\rangle & \langle b_2|a_2\rangle & \cdots\\ \vdots & \vdots & \ddots\end{pmatrix}\begin{pmatrix}a_1 & 0 & \cdots\\ 0 & a_2 & \cdots\\ \vdots & \vdots & \ddots\end{pmatrix}\begin{pmatrix}\langle a_1|b_1\rangle & \langle a_1|b_2\rangle & \cdots\\ \langle a_2|b_1\rangle & \langle a_2|b_2\rangle & \cdots\\ \vdots & \vdots & \ddots\end{pmatrix}\end{aligned}$$

从而记幺正矩阵$\boldsymbol{U}=\begin{pmatrix}\langle b_1|a_1\rangle & \langle b_1|a_2\rangle & \cdots\\ \langle b_2|a_1\rangle & \langle b_2|a_2\rangle & \cdots\\ \vdots & \vdots & \ddots\end{pmatrix}$，则有$\tilde{\boldsymbol{A}}=\boldsymbol{U}\boldsymbol{A}\boldsymbol{U}^\dagger$，同理有$f(\tilde{\boldsymbol{A}})=\boldsymbol{U}f(\boldsymbol{A})\boldsymbol{U}^\dagger$，因此只要将本征矩阵对角化，并推出相应的幺正矩阵，即可得到$f(\hat{A})$在另一态矢上的矩阵形式。

（本题的解答）我们若以$|S_y\pm\rangle$为本征态，则$\boldsymbol{S}_y'=\frac{\hbar}{2}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}$；若以$|S_z\pm\rangle$为本征态，则$\boldsymbol{S}_y=\frac{\hbar}{2}\begin{pmatrix}0 & -\mathrm{i}\\ \mathrm{i} & 0\end{pmatrix}$。结合两种基矢的关系$|S_y\pm\rangle=\frac{1}{\sqrt{2}}(|S_z+\rangle\pm\mathrm{i}|S_z-\rangle)$，得$\boldsymbol{U}=\frac{1}{\sqrt{2}}\begin{pmatrix}1 & 1\\ \mathrm{i} & -\mathrm{i}\end{pmatrix}$，此时$\boldsymbol{S}_y=\boldsymbol{U}\boldsymbol{S}_y'\boldsymbol{U}^\dagger$，或写作$-\frac{\mathrm{i}}{\hbar}\boldsymbol{S}_y\theta=\boldsymbol{U}(-\frac{\mathrm{i}}{\hbar}\boldsymbol{S}_y'\theta)\boldsymbol{U}^\dagger$，因此：

$$\begin{aligned}\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}\boldsymbol{S}_y\theta}&=\boldsymbol{U}\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}\boldsymbol{S}_y'\theta}\boldsymbol{U}^\dagger=\frac{1}{\sqrt{2}}\begin{pmatrix}1 & 1\\ \mathrm{i} & -\mathrm{i}\end{pmatrix}\cdot\begin{pmatrix}\mathrm{e}^{-\frac{\mathrm{i}\theta}{2}} & 0\\ 0 & \mathrm{e}^{\frac{\mathrm{i}\theta}{2}}\end{pmatrix}\cdot\frac{1}{\sqrt{2}}\begin{pmatrix}1 & -\mathrm{i}\\ 1 & \mathrm{i}\end{pmatrix}=\frac{1}{2}\begin{pmatrix}\mathrm{e}^{-\frac{\mathrm{i}\theta}{2}}+\mathrm{e}^{\frac{\mathrm{i}\theta}{2}} & -\mathrm{i}(\mathrm{e}^{-\frac{\mathrm{i}\theta}{2}}-\mathrm{e}^{\frac{\mathrm{i}\theta}{2}})\\ \mathrm{i}(\mathrm{e}^{-\frac{\mathrm{i}\theta}{2}}-\mathrm{e}^{\frac{\mathrm{i}\theta}{2}}) & \mathrm{e}^{-\frac{\mathrm{i}\theta}{2}}+\mathrm{e}^{\frac{\mathrm{i}\theta}{2}}\end{pmatrix}\\
&=\frac{1}{2}\begin{pmatrix}2\cos\frac{\theta}{2} & -\mathrm{i}\cdot(-2\mathrm{i}\sin\frac{\theta}{2})\\ \mathrm{i}\cdot(-2\mathrm{i}\sin\frac{\theta}{2}) & 2\cos\frac{\theta}{2}\end{pmatrix}=\begin{pmatrix}\cos\frac{\theta}{2} & -\sin\frac{\theta}{2}\\ \sin\frac{\theta}{2} & \cos\frac{\theta}{2}\end{pmatrix}\end{aligned}$$

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

$\underbrace{[\frac{\mathrm{i}}{\hbar}\hat{S}_z\phi,[\dots,[\frac{\mathrm{i}}{\hbar}\hat{S}_z\phi,\hat{S}_x]]]}_{2p\text{层对易符号}}=(-1)^p\phi^{2p}\hat{S}_x$，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：

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

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：

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

练习5：推导$\frac{d^2}{dt^2}\langle\hat{B}\rangle(t)=\frac{1}{(\mathrm{i}\hbar)^2}\langle u(t)|[[\hat{B},\hat{H}],\hat{H}]|u(t)\rangle$

证明：我们知道，对$\langle\hat{B}\rangle(t)=\langle u(t)|\hat{B}|u(t)\rangle$做一次求导，得$\frac{d}{dt}\langle\hat{B}\rangle(t)=\frac{1}{\mathrm{i}\hbar}\langle[\hat{B},\hat{H}]\rangle(t)$，接下来我们再做一次求导，得：

$$\begin{aligned}\frac{d^2}{dt^2}\langle\hat{B}\rangle(t)&=\frac{d}{dt}[\frac{d}{dt}\langle\hat{B}\rangle(t)]=\frac{d}{dt}[\frac{1}{\mathrm{i}\hbar}\langle[\hat{B},\hat{H}]\rangle(t)]=\frac{1}{\mathrm{i}\hbar}\frac{d}{dt}[\langle u(t)|[\hat{B},\hat{H}]|u(t)\rangle]=\frac{1}{\mathrm{i}\hbar}\frac{d}{dt}[\langle u(0)|\mathrm{e}^{\frac{\mathrm{i}}{\hbar}\hat{H}t}[\hat{B},\hat{H}]\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}\hat{H}t}|u(0)\rangle]\\&=\frac{1}{\mathrm{i}\hbar}[\langle u(0)|\mathrm{e}^{\frac{\mathrm{i}}{\hbar}\hat{H}t}(\frac{\mathrm{i}}{\hbar}\hat{H})[\hat{B},\hat{H}]\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}\hat{H}t}|u(0)\rangle+\langle u(0)|\mathrm{e}^{\frac{\mathrm{i}}{\hbar}\hat{H}t}[\hat{B},\hat{H}](-\frac{\mathrm{i}}{\hbar}\hat{H})\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}\hat{H}t}|u(0)\rangle]\\&=\frac{1}{\mathrm{i}\hbar}\cdot(-\frac{\mathrm{i}}{\hbar})[-\langle u(t)|\hat{H}[\hat{B},\hat{H}]|u(t)\rangle+\langle u(t)|[\hat{B},\hat{H}]\hat{H}|u(t)\rangle]=\frac{1}{(\mathrm{i}\hbar)^2}\langle u(t)|([\hat{B},\hat{H}]\hat{H}-\hat{H}[\hat{B},\hat{H}])|u(t)\rangle\\&=\frac{1}{(\mathrm{i}\hbar)^2}\langle u(t)|[[\hat{B},\hat{H}],\hat{H}]|u(t)\rangle\end{aligned}$$

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

$$\boldsymbol{S}_x=\frac{\hbar}{2}\begin{pmatrix}0&1\\1&0\end{pmatrix}\quad\boldsymbol{S}_y=\frac{\hbar}{2}\begin{pmatrix}0&-\mathrm{i}\\\mathrm{i}&0\end{pmatrix}\quad\boldsymbol{S}_z=\frac{\hbar}{2}\begin{pmatrix}1&0\\0&-1\end{pmatrix}\quad\boldsymbol{S}_+=\hbar\begin{pmatrix}0&1\\0&0\end{pmatrix}\quad\boldsymbol{S}_-=\hbar\begin{pmatrix}0&0\\1&0\end{pmatrix}$$

解：记$|S_z+\rangle\equiv|\alpha\rangle$，$|S_z-\rangle\equiv|\beta\rangle$，则自旋算符满足如下关系：（1）$\hat{S}_z|\alpha\rangle=\frac{\hbar}{2}|\alpha\rangle$，$\hat{S}_z|\beta\rangle=-\frac{\hbar}{2}|\beta\rangle$；（2）$\hat{S}_+|\alpha\rangle=\mathbf{0}$，$\hat{S}_+|\beta\rangle=\hbar|\beta\rangle$；（3）$\hat{S}_-|\alpha\rangle=\hbar|\alpha\rangle$，$\hat{S}_-|\beta\rangle=\mathbf{0}$；（4）$\hat{S}_x=\frac{1}{2}(\hat{S}_++\hat{S}_-)$，$\hat{S}_y=\frac{1}{2\mathrm{i}}(\hat{S}_+-\hat{S}_-)$。因此计算矩阵元得：

$$\langle\alpha|\hat{S}_x|\alpha\rangle=\frac{1}{2}(\langle\alpha|\hat{S}_+|\alpha\rangle+\langle\alpha|\hat{S}_-|\alpha\rangle)=\frac{1}{2}(\langle\alpha|\cdot\mathbf{0}+\langle\alpha|\cdot\hbar|\beta\rangle)=0$$
$$\langle\alpha|\hat{S}_x|\beta\rangle=\frac{1}{2}(\langle\alpha|\hat{S}_+|\beta\rangle+\langle\alpha|\hat{S}_-|\beta\rangle)=\frac{1}{2}(\langle\alpha|\cdot\hbar|\alpha\rangle+\langle\alpha|\cdot\mathbf{0})=\frac{\hbar}{2}$$
$$\langle\beta|\hat{S}_x|\alpha\rangle=\frac{1}{2}(\langle\beta|\hat{S}_+|\alpha\rangle+\langle\beta|\hat{S}_-|\alpha\rangle)=\frac{1}{2}(\langle\beta|\cdot\mathbf{0}+\langle\beta|\cdot\hbar|\beta\rangle)=\frac{\hbar}{2}$$
$$\langle\beta|\hat{S}_x|\beta\rangle=\frac{1}{2}(\langle\beta|\hat{S}_+|\beta\rangle+\langle\beta|\hat{S}_-|\beta\rangle)=\frac{1}{2}(\langle\beta|\cdot\hbar|\alpha\rangle+\langle\beta|\cdot\mathbf{0})=0$$

$$\langle\alpha|\hat{S}_y|\alpha\rangle=\frac{1}{2\mathrm{i}}(\langle\alpha|\hat{S}_+|\alpha\rangle-\langle\alpha|\hat{S}_-|\alpha\rangle)=\frac{1}{2\mathrm{i}}(\langle\alpha|\cdot\mathbf{0}-\langle\alpha|\cdot\hbar|\beta\rangle)=0$$
$$\langle\alpha|\hat{S}_y|\beta\rangle=\frac{1}{2\mathrm{i}}(\langle\alpha|\hat{S}_+|\beta\rangle-\langle\alpha|\hat{S}_-|\beta\rangle)=\frac{1}{2\mathrm{i}}(\langle\alpha|\cdot\hbar|\alpha\rangle-\langle\alpha|\cdot\mathbf{0})=-\frac{\mathrm{i}\hbar}{2}$$
$$\langle\beta|\hat{S}_y|\alpha\rangle=\frac{1}{2\mathrm{i}}(\langle\beta|\hat{S}_+|\alpha\rangle-\langle\beta|\hat{S}_-|\alpha\rangle)=\frac{1}{2\mathrm{i}}(\langle\beta|\cdot\mathbf{0}-\langle\beta|\cdot\hbar|\beta\rangle)=\frac{\mathrm{i}\hbar}{2}$$
$$\langle\beta|\hat{S}_y|\beta\rangle=\frac{1}{2\mathrm{i}}(\langle\beta|\hat{S}_+|\beta\rangle-\langle\beta|\hat{S}_-|\beta\rangle)=\frac{1}{2\mathrm{i}}(\langle\beta|\cdot\hbar|\alpha\rangle-\langle\beta|\cdot\mathbf{0})=0$$

$$\langle\alpha|\hat{S}_z|\alpha\rangle=\langle\alpha|\cdot\frac{\hbar}{2}|\alpha\rangle=\frac{\hbar}{2}\quad\langle\alpha|\hat{S}_z|\beta\rangle=\langle\alpha|\cdot(-\frac{\hbar}{2}|\beta\rangle)=\mathbf{0}\quad\langle\beta|\hat{S}_z|\alpha\rangle=\langle\beta|\cdot\frac{\hbar}{2}|\alpha\rangle=\mathbf{0}\quad\langle\beta|\hat{S}_z|\beta\rangle=\langle\beta|\cdot(-\frac{\hbar}{2}|\beta\rangle)=-\frac{\hbar}{2}$$

$$\langle\alpha|\hat{S}_+|\alpha\rangle=\langle\alpha|\cdot\mathbf{0}=\mathbf{0}\quad\langle\alpha|\hat{S}_+|\beta\rangle=\langle\alpha|\cdot\hbar|\alpha\rangle=\hbar\quad\langle\beta|\hat{S}_+|\alpha\rangle=\langle\beta|\cdot\mathbf{0}=\mathbf{0}\quad\langle\beta|\hat{S}_+|\beta\rangle=\langle\beta|\cdot\hbar|\alpha\rangle=\mathbf{0}$$

$$\langle\alpha|\hat{S}_-|\alpha\rangle=\langle\alpha|\cdot\hbar|\beta\rangle=\mathbf{0}\quad\langle\alpha|\hat{S}_-|\beta\rangle=\langle\alpha|\cdot\mathbf{0}=\mathbf{0}\quad\langle\beta|\hat{S}_-|\alpha\rangle=\langle\beta|\cdot\hbar|\beta\rangle=\hbar\quad\langle\beta|\hat{S}_-|\beta\rangle=\langle\beta|\cdot\mathbf{0}=\mathbf{0}$$

故原式成立

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

$$\begin{aligned}\widetilde{\psi}(\boldsymbol{p})&=(2\pi)^{-\frac{3}{2}}\int r^2dr\iint4\pi\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\mathrm{e}^{-\frac{\mathrm{i}\pi l}{2}}j_l(kr)[Y_l^m(\theta,\varphi)]^*Y_l^m(\theta_p,\varphi_p)f(r)Y_L^M(\theta,\varphi)\sin\theta d\varphi d\theta\\&=\sqrt{\frac{2}{\pi}}\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\mathrm{e}^{-\frac{\mathrm{i}\pi l}{2}}Y_l^m(\theta_p,\varphi_p)\int r^2j_l(pr)f(r)dr\iint[Y_l^m(\theta,\varphi)]^*Y_L^M(\theta,\varphi)\sin\theta d\varphi d\theta\\&=\sqrt{\frac{2}{\pi}}\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\mathrm{e}^{-\frac{\mathrm{i}\pi l}{2}}Y_l^m(\theta_p,\varphi_p)\int r^2j_l(pr)f(r)\delta_{mM}\delta_{lL}dr=\sqrt{\frac{2}{\pi}}\mathrm{e}^{-\frac{\mathrm{i}\pi L}{2}}Y_L^M(\theta_p,\varphi_p)\int r^2j_l(pr)f(r)dr\end{aligned}$$

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

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

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：

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

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$c_{\alpha\alpha}=\pm1$，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$c_{\beta\beta}=\pm1$，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4.5.17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$\hat{J}_y=\frac{1}{2\mathrm{i}}(\hat{J}_+-\hat{J}_-)$，因此有：

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

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

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

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

$$\begin{pmatrix}0&-\frac{\sqrt{2}}{2}&0\\\frac{\sqrt{2}}{2}&0&-\frac{\sqrt{2}}{2}\\0&\frac{\sqrt{2}}{2}&0\end{pmatrix}^3=\begin{pmatrix}-\frac{1}{2}&0&\frac{1}{2}\\0&-1&0\\\frac{1}{2}&0&-\frac{1}{2}\end{pmatrix}\begin{pmatrix}0&-\frac{\sqrt{2}}{2}&0\\\frac{\sqrt{2}}{2}&0&-\frac{\sqrt{2}}{2}\\0&\frac{\sqrt{2}}{2}&0\end{pmatrix}=-\begin{pmatrix}0&-\frac{\sqrt{2}}{2}&0\\\frac{\sqrt{2}}{2}&0&-\frac{\sqrt{2}}{2}\\0&\frac{\sqrt{2}}{2}&0\end{pmatrix}$$

$$\begin{pmatrix}0&-\frac{\sqrt{2}}{2}&0\\\frac{\sqrt{2}}{2}&0&-\frac{\sqrt{2}}{2}\\0&\frac{\sqrt{2}}{2}&0\end{pmatrix}^4=-\begin{pmatrix}0&-\frac{\sqrt{2}}{2}&0\\\frac{\sqrt{2}}{2}&0&-\frac{\sqrt{2}}{2}\\0&\frac{\sqrt{2}}{2}&0\end{pmatrix}\begin{pmatrix}0&-\frac{\sqrt{2}}{2}&0\\\frac{\sqrt{2}}{2}&0&-\frac{\sqrt{2}}{2}\\0&\frac{\sqrt{2}}{2}&0\end{pmatrix}=-\begin{pmatrix}-\frac{1}{2}&0&\frac{1}{2}\\0&-1&0\\\frac{1}{2}&0&-\frac{1}{2}\end{pmatrix}$$

$$\begin{pmatrix}0&-\frac{\sqrt{2}}{2}&0\\\frac{\sqrt{2}}{2}&0&-\frac{\sqrt{2}}{2}\\0&\frac{\sqrt{2}}{2}&0\end{pmatrix}^5=-\begin{pmatrix}-\frac{1}{2}&0&\frac{1}{2}\\0&-1&0\\\frac{1}{2}&0&-\frac{1}{2}\end{pmatrix}\begin{pmatrix}0&-\frac{\sqrt{2}}{2}&0\\\frac{\sqrt{2}}{2}&0&-\frac{\sqrt{2}}{2}\\0&\frac{\sqrt{2}}{2}&0\end{pmatrix}=\begin{pmatrix}0&-\frac{\sqrt{2}}{2}&0\\\frac{\sqrt{2}}{2}&0&-\frac{\sqrt{2}}{2}\\0&\frac{\sqrt{2}}{2}&0\end{pmatrix}$$

因此我们有$\begin{pmatrix}0&-\frac{\sqrt{2}}{2}&0\\\frac{\sqrt{2}}{2}&0&-\frac{\sqrt{2}}{2}\\0&\frac{\sqrt{2}}{2}&0\end{pmatrix}^{2p-1}=(-1)^{p-1}\begin{pmatrix}0&-\frac{\sqrt{2}}{2}&0\\\frac{\sqrt{2}}{2}&0&-\frac{\sqrt{2}}{2}\\0&\frac{\sqrt{2}}{2}&0\end{pmatrix}$，$\begin{pmatrix}0&-\frac{\sqrt{2}}{2}&0\\\frac{\sqrt{2}}{2}&0&-\frac{\sqrt{2}}{2}\\0&\frac{\sqrt{2}}{2}&0\end{pmatrix}^{2p}=(-1)^{p-1}\begin{pmatrix}-\frac{1}{2}&0&\frac{1}{2}\\0&-1&0\\\frac{1}{2}&0&-\frac{1}{2}\end{pmatrix}$，其中$p\in\mathbb{N}^+$，代入原式得：

$$\begin{aligned}
\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}J_y\theta}&=1+\sum_{k=1}^{\infty}\frac{\theta^k}{k!}\begin{pmatrix}0&-\frac{\sqrt{2}}{2}&0\\\frac{\sqrt{2}}{2}&0&-\frac{\sqrt{2}}{2}\\0&\frac{\sqrt{2}}{2}&0\end{pmatrix}^k=1+\sum_{k=1}^{\infty}\frac{\theta^{2k-1}}{(2k-1)!}\begin{pmatrix}0&-\frac{\sqrt{2}}{2}&0\\\frac{\sqrt{2}}{2}&0&-\frac{\sqrt{2}}{2}\\0&\frac{\sqrt{2}}{2}&0\end{pmatrix}^{2k-1}+\sum_{k=1}^{\infty}\frac{\theta^{2k}}{(2k)!}\begin{pmatrix}0&-\frac{\sqrt{2}}{2}&0\\\frac{\sqrt{2}}{2}&0&-\frac{\sqrt{2}}{2}\\0&\frac{\sqrt{2}}{2}&0\end{pmatrix}^{2k}\\
&=1+\sum_{k=1}^{\infty}\frac{(-1)^{k-1}\theta^{2k-1}}{(2k-1)!}\begin{pmatrix}0&-\frac{\sqrt{2}}{2}&0\\\frac{\sqrt{2}}{2}&0&-\frac{\sqrt{2}}{2}\\0&\frac{\sqrt{2}}{2}&0\end{pmatrix}+\sum_{k=1}^{\infty}\frac{(-1)^{k-1}\theta^{2k}}{(2k)!}\begin{pmatrix}-\frac{1}{2}&0&\frac{1}{2}\\0&-1&0\\\frac{1}{2}&0&-\frac{1}{2}\end{pmatrix}\\
&=\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}+\begin{pmatrix}-\frac{1}{2}&0&\frac{1}{2}\\0&-1&0\\\frac{1}{2}&0&-\frac{1}{2}\end{pmatrix}+\sum_{k=1}^{\infty}\frac{(-1)^{k-1}\theta^{2k-1}}{(2k-1)!}\begin{pmatrix}0&-\frac{\sqrt{2}}{2}&0\\\frac{\sqrt{2}}{2}&0&-\frac{\sqrt{2}}{2}\\0&\frac{\sqrt{2}}{2}&0\end{pmatrix}+\sum_{k=0}^{\infty}\frac{(-1)^{k-1}\theta^{2k}}{(2k)!}\begin{pmatrix}-\frac{1}{2}&0&\frac{1}{2}\\0&-1&0\\\frac{1}{2}&0&-\frac{1}{2}\end{pmatrix}\\
&=\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}+\begin{pmatrix}-\frac{1}{2}&0&\frac{1}{2}\\0&-1&0\\\frac{1}{2}&0&-\frac{1}{2}\end{pmatrix}+\sin\theta\begin{pmatrix}0&-\frac{\sqrt{2}}{2}&0\\\frac{\sqrt{2}}{2}&0&-\frac{\sqrt{2}}{2}\\0&\frac{\sqrt{2}}{2}&0\end{pmatrix}-\cos\theta\begin{pmatrix}-\frac{1}{2}&0&\frac{1}{2}\\0&-1&0\\\frac{1}{2}&0&-\frac{1}{2}\end{pmatrix}\\
&=\begin{pmatrix}\frac{1+\cos\theta}{2}&-\frac{\sqrt{2}\sin\theta}{2}&\frac{1-\cos\theta}{2}\\\frac{\sqrt{2}\sin\theta}{2}&\cos\theta&-\frac{\sqrt{2}\sin\theta}{2}\\\frac{1-\cos\theta}{2}&\frac{\sqrt{2}\sin\theta}{2}&\frac{1+\cos\theta}{2}\end{pmatrix}
\end{aligned}$$

最终我们得到$\boldsymbol{D}^1(\phi,\theta,\chi)$的表达式：

$$\boldsymbol{D}^1(\phi,\theta,\chi)=\begin{pmatrix}\mathrm{e}^{-\mathrm{i}\phi}&0&0\\0&1&0\\0&0&\mathrm{e}^{\mathrm{i}\phi}\end{pmatrix}\begin{pmatrix}\frac{1+\cos\theta}{2}&-\frac{\sqrt{2}\sin\theta}{2}&\frac{1-\cos\theta}{2}\\\frac{\sqrt{2}\sin\theta}{2}&\cos\theta&-\frac{\sqrt{2}\sin\theta}{2}\\\frac{1-\cos\theta}{2}&\frac{\sqrt{2}\sin\theta}{2}&\frac{1+\cos\theta}{2}\end{pmatrix}\begin{pmatrix}\mathrm{e}^{-\mathrm{i}\chi}&0&0\\0&1&0\\0&0&\mathrm{e}^{\mathrm{i}\chi}\end{pmatrix}$$
$$=\begin{pmatrix}\frac{1+\cos\theta}{2}\mathrm{e}^{-\mathrm{i}(\phi+\chi)}&-\frac{\sqrt{2}\sin\theta}{2}\mathrm{e}^{-\mathrm{i}\phi}&\frac{1-\cos\theta}{2}\mathrm{e}^{-\mathrm{i}(\phi-\chi)}\\\frac{\sqrt{2}\sin\theta}{2}\mathrm{e}^{-\mathrm{i}\chi}&\cos\theta&-\frac{\sqrt{2}\sin\theta}{2}\mathrm{e}^{\mathrm{i}\chi}\\\frac{1-\cos\theta}{2}\mathrm{e}^{-\mathrm{i}(-\phi+\chi)}&\frac{\sqrt{2}\sin\theta}{2}\mathrm{e}^{\mathrm{i}\phi}&\frac{1+\cos\theta}{2}\mathrm{e}^{\mathrm{i}(\phi+\chi)}\end{pmatrix}$$

作为对比，三维空间的旋转矩阵表达式为：

$$\boldsymbol{R}(\phi,\theta,\chi)=\begin{pmatrix}\cos\phi\cos\theta\cos\chi-\sin\phi\sin\chi&-\cos\phi\cos\theta\sin\chi-\sin\phi\cos\chi&\cos\phi\cos\theta\\\sin\phi\cos\theta\cos\chi+\cos\phi\sin\chi&-\sin\phi\cos\theta\sin\chi+\cos\phi\cos\chi&\sin\phi\sin\theta\\-\sin\theta\cos\chi&\sin\theta\sin\chi&\cos\theta\end{pmatrix}$$

以绕z轴一周为例，此时$\begin{cases}\phi=2\pi\\\theta=0\\\chi=0\end{cases}$，代入得$\boldsymbol{D}^1(2\pi,0,0)=\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}=\boldsymbol{I}$，$\boldsymbol{R}(2\pi,0,0)=\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}=\boldsymbol{I}$。可以证明，这两种表示矩阵满足同构表示的关系。

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）：

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

对第一个式子两边使用总降算符$\hat{J}_-$，得：

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

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

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：

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

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

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

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

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:

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

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

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:

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

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

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

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

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

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