课堂练习

练习1: 证明旋轨耦合中

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

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 $\begin{cases} a=\sqrt{\frac{1}{3}}\\ b=-\sqrt{\frac{2}{3}} \end{cases}$,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
$$m{R}_x(arepsilon)m{R}_y(arepsilon)-m{R}_y(arepsilon)m{R}_x(arepsilon)=m{R}_z(arepsilon^2)-m{I}$$

证明:根据定义,旋转矩阵展开至二阶项时的形式为:

$$m{R}_x(arepsilon) = egin{bmatrix} 1 & 0 & 0 \ 0 & 1 - rac{arepsilon^2}{2} & -arepsilon \ 0 & arepsilon & 1 - rac{arepsilon^2}{2} \end{bmatrix} \quad m{R}_y(arepsilon) = egin{bmatrix} 1 - rac{arepsilon^2}{2} & 0 & arepsilon \ 0 & 1 & 0 \ -arepsilon & 0 & 1 - rac{arepsilon^2}{2} \end{bmatrix} \quad m{R}_z(arepsilon) = egin{bmatrix} 1 - rac{arepsilon^2}{2} & -arepsilon & 0 \ arepsilon & 1 - rac{arepsilon^2}{2} & 0 \ 0 & 0 & 1 \end{bmatrix}$$

作矩阵乘法得:

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

两项相减,并忽略三次及更高次项,得:

$$m{R}_x(arepsilon)m{R}_y(arepsilon) - m{R}_y(arepsilon)m{R}_x(arepsilon) = egin{bmatrix} 0 & -arepsilon^2 & rac{arepsilon^3}{2} \ rac{arepsilon^3}{2} & rac{arepsilon^3}{2} & 0 \end{bmatrix} \simeq egin{bmatrix} 0 & -arepsilon^2 & 0 \ arepsilon^2 & 0 & 0 \ 0 & 0 & 0 \end{bmatrix}$$

又

$$m{R}_z(arepsilon^2) - m{I} = egin{bmatrix} 1 - rac{arepsilon^4}{2} & -arepsilon^2 & 0 \ arepsilon^2 & 1 - rac{arepsilon^4}{2} & 0 \ 0 & 0 & 1 \end{bmatrix} - egin{bmatrix} 1 & 0 & 0 \ 0 & 1 & 0 \ 0 & 0 & 1 \end{bmatrix} = egin{bmatrix} -rac{arepsilon^4}{2} & -arepsilon^2 & 0 \ arepsilon^2 & -rac{arepsilon^4}{2} & 0 \ 0 & 0 & 0 \end{bmatrix} \simeq egin{bmatrix} 0 & -arepsilon^2 & 0 \ arepsilon^2 & 0 & 0 \ 0 & 0 & 0 \end{bmatrix}$$

因此
$$m{R}_x(arepsilon)m{R}_y(arepsilon)-m{R}_y(arepsilon)m{R}_x(arepsilon)=m{R}_z(arepsilon^2)-m{I}$$
,原题得证

练习3: 是否有其他方式来推导4.6.7的结论(即 $\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}S_y heta}=egin{pmatrix}\cosrac{ heta}{2}&-\sinrac{ heta}{2}\\\sinrac{ heta}{2}&\cosrac{ heta}{2}\end{pmatrix}$)?

解:

第四章习题

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

$$oldsymbol{S}_x = rac{\hbar}{2}egin{pmatrix} 0 & 1 \ 1 & 0 \end{pmatrix} \quad oldsymbol{S}_y = rac{\hbar}{2}egin{pmatrix} 0 & -\mathrm{i} \ \mathrm{i} & 0 \end{pmatrix} \quad oldsymbol{S}_z = rac{\hbar}{2}egin{pmatrix} 1 & 0 \ 0 & -1 \end{pmatrix} \quad oldsymbol{S}_+ = \hbaregin{pmatrix} 0 & 1 \ 0 & 0 \end{pmatrix} \quad oldsymbol{S}_- = \hbaregin{pmatrix} 0 & 0 \ 1 & 0 \end{pmatrix}$$

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 $\psi({\bf r})=\psi(r,\theta,\varphi)=f(r)Y_L^M(\theta,\varphi)$,则经傅里叶变换后,波函数在动量空间表象的形式为:

$$\widetilde{\psi}(oldsymbol{p}) = (2\pi)^{-rac{3}{2}} \iiint \mathrm{e}^{-\mathrm{i}oldsymbol{p}\cdotoldsymbol{r}} f(r) Y_L^M(heta,arphi) r^2 \sin heta dr darphi d heta$$

又平面波按球谐函数展开之后为:

$$\mathrm{e}^{-\mathrm{i}oldsymbol{p}\cdotoldsymbol{r}}=4\pi\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\mathrm{e}^{-rac{\mathrm{i}\pi l}{2}}j_{l}(kr)[Y_{l}^{m}(heta,arphi)]^{st}Y_{l}^{m}(heta_{p},arphi_{p})$$

因此代入得

$$egin{aligned} \widetilde{\psi}(oldsymbol{p}) &= (2\pi)^{-rac{3}{2}} \int r^2 dr \iint 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \mathrm{e}^{-rac{\mathrm{i}\pi l}{2}} j_l(kr) [Y_l^m(heta,arphi)]^* Y_l^m(heta_p,arphi_p) f(r) Y_L^M(heta,arphi) \sin heta darphi d heta \ &= \sqrt{rac{2}{\pi}} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \mathrm{e}^{-rac{\mathrm{i}\pi l}{2}} Y_l^m(heta_p,arphi_p) \int r^2 j_l(pr) f(r) dr \iint [Y_l^m(heta,arphi)]^* Y_L^M(heta,arphi) \sin heta darphi d heta \ &= \sqrt{rac{2}{\pi}} \sum_{m=-l}^{\infty} \sum_{m=-l}^{l} \mathrm{e}^{-rac{\mathrm{i}\pi l}{2}} Y_l^m(heta_p,arphi_p) \int r^2 j_l(pr) f(r) \delta_{mM} \delta_{lL} dr = \sqrt{rac{2}{\pi}} \mathrm{e}^{-rac{\mathrm{i}\pi L}{2}} Y_L^M(heta_p,arphi_p) \int r^2 j_l(pr) f(r) dr \end{aligned}$$

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 $\hat{H}=A\hat{S}_1\cdot\hat{S}_2$,式中A为常数。求出 $\hat{H}=A\hat{S}_1\cdot\hat{S}_2$, $\hat{S}^2=(\hat{S}_1+\hat{S}_2)^2$, $\hat{S}_z=\hat{S}_{z,1}+\hat{S}_{z,2}$ 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 $S_z=\hbaregin{pmatrix}1&0&0&0\\0&0&0&0\\0&0&0&0\\0&0&0&-1\end{pmatrix}$,

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

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

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 $m{H}=rac{A\hbar^2}{4}egin{pmatrix}1&0&0&0\0&-1&2&0\0&2&-1&0\0&0&0&1\end{pmatrix}$

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

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

因此 \hat{S}^2 作用在未耦合表象的效果为:

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

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

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a,b分别与 $\hat{\pmb{S}}^2,\hat{S}_z$ 作用在耦合表象的态矢时得到的本征值有关:

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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:

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

证明:由于
$$\hat{m L}=\hat{m r} imes\hat{m p}=egin{array}{cccc} \hat{m i} & \hat{m j} & \hat{m k} \\ \hat{r}_x & \hat{r}_y & \hat{r}_z \\ \hat{p}_x & \hat{p}_y & \hat{p}_z \\ \end{array}$$
,而 $\hat{m r}^2=\hat{r}_x^2+\hat{r}_y^2+\hat{r}_z^2$, $\hat{m p}^2=\hat{p}_x^2+\hat{p}_y^2+\hat{p}_z^2$, $\hat{m r}\cdot\hat{m p}=\hat{r}_x\hat{p}_x+\hat{r}_y\hat{p}_y+\hat{r}_z\hat{p}_z$,因此有:

$$\begin{split} \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) \hat{p}_z + \hat{r}_z \hat{p}_y \hat{r}_z \hat{p}_y) + (\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}_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}_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] \\ &+ [\hat{r}_z \hat{r}_z \hat{p}_x \hat{p}_x + \hat{r}_x ([\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] \\ &+ [\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}_x, \hat{p}_x] - \hat{r}_x \hat{p}_x) \hat{p}_y + \hat{r}_y \hat{p}_y \hat{p}_x \hat{p}_x] \\ &= [\hat{r}_y^2 \hat{p}_z^2 + \hat{r}_y (i \hat{h} - \hat{r}_z \hat{p}_z) \hat{p}_y + \hat{r}_z (i \hat{h} - \hat{r}_y \hat{p}_y) \hat{p}_x + \hat{r}_z (\hat{p}_x \hat{p}_y) \hat{p}_z + \hat{r}_z \hat{p}_y^2) \hat{p}_x + \hat{r}_x \hat{r}_y \hat{p}_y \hat{p}_x \hat{p}_x \hat{p}_z \\ &+ [\hat{r}_x^2 \hat{p}_y^2 + \hat{r}_x (i \hat{h} - \hat{r}_y \hat{p}_y) \hat{p}_x + \hat{r}_y (i \hat{h} - \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 (i \hat{h} - \hat{r}_z \hat{p}_z) \hat{p}_y + \hat{r}_z (i \hat{h} - \hat{r}_y \hat{p}_y) \hat{p}_x + \hat{r}_z^2 \hat{p}_y^2) \\ &+ [\hat{r}_x^2 \hat{p}_y^2 + \hat{r}_x (i \hat{h} - \hat{r}_y \hat{p}_y) \hat{p}_x + \hat{r}_z^2 \hat{p}_y^2) \\ &+ [\hat{r}_x^2 \hat{p}_y^2 + \hat{r}_x \hat{r}_y \hat{p}_y \hat{p}_x + \hat{r}_z^2 \hat{p}_y^2) \\ &+ [\hat{r}_x^2 \hat{p}_y^2 + \hat{r}_x \hat{r}_y \hat{p}_y \hat{p}_x + \hat{r}_z^2 \hat{p}_y^2] \\ &+ [\hat{r}_x^2 \hat{p}_y^2 + \hat{r}_x \hat{r}_y \hat{p}_y \hat{p}_x + \hat{r}_z^2 \hat{p}_y^2] \\ &+ [\hat{r}_x^2 \hat{p}_y^2 + \hat{r}_x \hat{r}_y \hat{p}_y \hat{p}_x + \hat{r}_y^2 \hat{p}_y^2) \\ &$$

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:

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

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

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

所表示的耦合表象本征态|jm;ls angle表达式

解:首先我们知道 $|l-s| \leq j \leq l+s$,代入得 $\frac{3}{2} \leq j \leq \frac{5}{2}$ (实际上j只能取 $\frac{5}{2}$ 或 $\frac{3}{2}$)。其次, $-\frac{5}{2} = -2 - \frac{1}{2} \leq m + m_s \leq 2 + \frac{1}{2} = \frac{5}{2}$,即 $-(l+s) \leq m + m_s \leq l+s$ 。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):

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

对第一个式子两边使用总降算符 \hat{J}_- ,得:

$$\hat{J}_{-}|j=rac{5}{2},m_{c}=rac{5}{2}
angle =\sqrt{rac{5}{2}(rac{5}{2}+1)-rac{5}{2}(rac{5}{2}-1)}\hbar|j=rac{5}{2},m_{c}=rac{3}{2}
angle =\sqrt{5}\hbar|j=rac{5}{2},m_{c}=rac{3}{2}
angle$$

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

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

$$\hat{J}_{-}|j=rac{5}{2},m_{c}=rac{3}{2}
angle =\sqrt{rac{5}{2}(rac{5}{2}+1)-rac{3}{2}(rac{3}{2}-1)}\hbar|j=rac{5}{2},m_{c}=rac{1}{2}
angle =2\sqrt{2}\hbar|j=rac{5}{2},m_{c}=rac{1}{2}
angle$$

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

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

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

从而有 $|j=\frac{5}{2},m_c=\frac{1}{2}
angle=\sqrt{\frac{3}{5}}\hbar|m=0,m_s=\frac{1}{2}
angle+\sqrt{\frac{2}{5}}|m=1,m_s=-\frac{1}{2}
angle$ 对第二个式子两边使用总升算符 \hat{J}_+ ,得:

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

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

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

$$\hat{J}_{+}|j=rac{5}{2},m_{c}=-rac{3}{2}
angle =\sqrt{rac{5}{2}(rac{5}{2}+1)-(-rac{3}{2})(-rac{3}{2}+1)}\hbar|j=rac{5}{2},m_{c}=-rac{1}{2}
angle =2\sqrt{2}\hbar|j=rac{5}{2},m_{c}=-rac{1}{2}
angle$$

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

$$egin{split} \hat{J}_{+}|m=-2,m_{s}=rac{1}{2}
angle &=(\hat{L}_{+}+\hat{S}_{+})|m=-2,m_{s}=rac{1}{2}
angle &=\hat{L}_{+}|m=-2,m_{s}=rac{1}{2}
angle +\hat{S}_{+}|m=-2,m_{s}=rac{1}{2}
angle &=\sqrt{2(2+1)-(-2)(-2+1)}\hbar|m=-1,m_{s}=rac{1}{2}
angle +0=2\hbar|m=-1,m_{s}=rac{1}{2}
angle &=0, \end{split}$$

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

从而有 $|j=rac{5}{2},m_c=-rac{1}{2}
angle=\sqrt{rac{3}{5}}\hbar|m=0,m_s=-rac{1}{2}
angle+\sqrt{rac{2}{5}}|m=-1,m_s=rac{1}{2}
angle$ 接下来讨论 $j=rac{3}{2}$ 的情形,此时 $m=\pmrac{3}{2},\pmrac{1}{2}$,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

$$\left\{egin{array}{l} c_1=\sqrt{rac{1}{5}},c_2=-\sqrt{rac{4}{5}}\ c_3=\sqrt{rac{2}{5}},c_4=-\sqrt{rac{3}{5}}\ c_5=\sqrt{rac{2}{5}},c_6=-\sqrt{rac{3}{5}}\ c_7=\sqrt{rac{1}{5}},c_8=-\sqrt{rac{4}{5}} \end{array}
ight.$$

因此有

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