

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

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

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

练习2: 证明 $R_x(\varepsilon)R_y(\varepsilon) - R_y(\varepsilon)R_x(\varepsilon) = R_z(\varepsilon^2) - I$

证明: 根据定义, 旋转矩阵展开至二阶项时的形式为:

$$R_x(\varepsilon) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 - \frac{\varepsilon^2}{2} & -\varepsilon \\ 0 & \varepsilon & 1 - \frac{\varepsilon^2}{2} \end{bmatrix} \quad R_y(\varepsilon) = \begin{bmatrix} 1 - \frac{\varepsilon^2}{2} & 0 & \varepsilon \\ 0 & 1 & 0 \\ -\varepsilon & 0 & 1 - \frac{\varepsilon^2}{2} \end{bmatrix} \quad R_z(\varepsilon) = \begin{bmatrix} 1 - \frac{\varepsilon^2}{2} & -\varepsilon & 0 \\ \varepsilon & 1 - \frac{\varepsilon^2}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

作矩阵乘法得:

$$\begin{aligned} R_x(\varepsilon)R_y(\varepsilon) &= \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 - \frac{\varepsilon^2}{2} & -\varepsilon \\ 0 & \varepsilon & 1 - \frac{\varepsilon^2}{2} \end{bmatrix} \begin{bmatrix} 1 - \frac{\varepsilon^2}{2} & 0 & \varepsilon \\ 0 & 1 & 0 \\ -\varepsilon & 0 & 1 - \frac{\varepsilon^2}{2} \end{bmatrix} = \begin{bmatrix} 1 - \frac{\varepsilon^2}{2} & 0 & \varepsilon \\ \varepsilon^2 & 1 - \frac{\varepsilon^2}{2} & -\varepsilon(1 - \frac{\varepsilon^2}{2}) \\ -\varepsilon(1 - \frac{\varepsilon^2}{2}) & \varepsilon & (1 - \frac{\varepsilon^2}{2})^2 \end{bmatrix} \\ R_y(\varepsilon)R_x(\varepsilon) &= \begin{bmatrix} 1 - \frac{\varepsilon^2}{2} & 0 & \varepsilon \\ 0 & 1 & 0 \\ -\varepsilon & 0 & 1 - \frac{\varepsilon^2}{2} \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 - \frac{\varepsilon^2}{2} & -\varepsilon \\ 0 & \varepsilon & 1 - \frac{\varepsilon^2}{2} \end{bmatrix} = \begin{bmatrix} 1 - \frac{\varepsilon^2}{2} & \varepsilon^2 & \varepsilon(1 - \frac{\varepsilon^2}{2}) \\ 0 & 1 - \frac{\varepsilon^2}{2} & -\varepsilon \\ -\varepsilon & \varepsilon(1 - \frac{\varepsilon^2}{2}) & (1 - \frac{\varepsilon^2}{2})^2 \end{bmatrix} \end{aligned}$$

两项相减, 并忽略三次及更高次项, 得:

$$R_x(\varepsilon)R_y(\varepsilon) - R_y(\varepsilon)R_x(\varepsilon) = \begin{bmatrix} 0 & -\varepsilon^2 & \frac{\varepsilon^3}{2} \\ \varepsilon^2 & 0 & \frac{\varepsilon^3}{2} \\ \frac{\varepsilon^3}{2} & \frac{\varepsilon^3}{2} & 0 \end{bmatrix} \simeq \begin{bmatrix} 0 & -\varepsilon^2 & 0 \\ \varepsilon^2 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

又

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

因此 $R_x(\varepsilon)R_y(\varepsilon) - R_y(\varepsilon)R_x(\varepsilon) = R_z(\varepsilon^2) - I$, 原题得证

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

解:

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

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

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

$$[\frac{i}{\hbar}\hat{S}_z\phi, [\frac{i}{\hbar}\hat{S}_z\phi, \hat{S}_x]] = [\frac{i}{\hbar}\hat{S}_z\phi, -\phi\hat{S}_y] = \frac{i\phi^2}{\hbar}[\hat{S}_z, \hat{S}_y] = \frac{i\phi^2}{\hbar} \cdot (-i\hbar\hat{S}_x) = \phi^2\hat{S}_x$$

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**

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

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

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

又平面波按球谐函数展开之后为:

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

因此代入得

$$\begin{aligned} \tilde{\psi}(\mathbf{p}) &= (2\pi)^{-\frac{3}{2}} \int r^2 dr \iint 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^l e^{-\frac{i\pi l}{2}} j_l(kr) [Y_l^m(\theta, \varphi)]^* Y_l^m(\theta_p, \varphi_p) f(r) Y_L^M(\theta, \varphi) \sin\theta d\varphi d\theta \\ &= \sqrt{\frac{2}{\pi}} \sum_{l=0}^{\infty} \sum_{m=-l}^l e^{-\frac{i\pi l}{2}} Y_l^m(\theta_p, \varphi_p) \int r^2 j_l(pr) f(r) dr \iint [Y_l^m(\theta, \varphi)]^* Y_L^M(\theta, \varphi) \sin\theta d\varphi d\theta \\ &= \sqrt{\frac{2}{\pi}} \sum_{l=0}^{\infty} \sum_{m=-l}^l e^{-\frac{i\pi l}{2}} Y_l^m(\theta_p, \varphi_p) \int r^2 j_l(pr) f(r) \delta_{mM} \delta_{lL} dr = \sqrt{\frac{2}{\pi}} e^{-\frac{i\pi L}{2}} Y_L^M(\theta_p, \varphi_p) \int r^2 j_L(pr) f(r) dr \end{aligned}$$

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:

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

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

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

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

因此 \hat{H} 作用在未耦合表象的效果为:

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

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

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

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

因此 \hat{S}^2 作用在未耦合表象的效果为:

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

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

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{S}^2, \hat{S}_z 作用在耦合表象的态矢时得到的本征值有关: $\hat{S}^2|ab\rangle = a(a+1)\hbar^2|ab\rangle \equiv R\hbar^2|ab\rangle$, $\hat{S}_z|ab\rangle = b\hbar|ab\rangle \equiv S\hbar|ab\rangle$, $\hat{H}|ab\rangle \equiv T\hbar^2|ab\rangle$, 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 $\hat{S}^2|00\rangle = 0 \cdot (0+1)\hbar^2|00\rangle = 0$,

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

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 $\hat{S}^2|11\rangle = 1 \cdot (1+1)\hbar^2|11\rangle = 2\hbar^2|11\rangle$ ， $\hat{S}_z|11\rangle = \hbar|11\rangle$ ， $\hat{H}|11\rangle = \frac{A}{4}\hbar^2|11\rangle$

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 $\hat{S}^2|1\bar{1}\rangle = 1 \cdot (1+1)\hbar^2|1\bar{1}\rangle = 2\hbar^2|1\bar{1}\rangle$ ， $\hat{S}_z|1\bar{1}\rangle = -\hbar|1\bar{1}\rangle$ ， $\hat{H}|1\bar{1}\rangle = \frac{A}{4}\hbar^2|1\bar{1}\rangle$

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 $\hat{S}^2|10\rangle = 1 \cdot (1+1)\hbar^2|10\rangle = 2\hbar^2|10\rangle$,

$$\hat{S}_z|10\rangle = 0\hbar|10\rangle = 0, \hat{H}|10\rangle = \frac{A}{4}\hbar^2|10\rangle$$

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:

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

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

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

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

故原题得证

另证: 由于 $\hat{L} = \hat{r} \times \hat{p}$, 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:

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

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，写出未耦合表象的基矢

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

所表示的耦合表象本征态 $|jm; ls\rangle$ 表达式

解：首先我们知道 $|l - s| \leq j \leq l + s$ ，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 ）：

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

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：

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

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

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

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

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

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:

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

解得

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

因此有

$$\left\{ \begin{array}{l} |j = \frac{3}{2}, m_c = \frac{3}{2} \rangle = \sqrt{\frac{1}{5}}|m = 1, m_s = \frac{1}{2} \rangle - \sqrt{\frac{4}{5}}|m = 2, m_s = -\frac{1}{2} \rangle \\ |j = \frac{3}{2}, m_c = \frac{1}{2} \rangle = \sqrt{\frac{2}{5}}|m = 0, m_s = \frac{1}{2} \rangle - \sqrt{\frac{3}{5}}|m = 1, m_s = -\frac{1}{2} \rangle \\ |j = \frac{3}{2}, m_c = -\frac{1}{2} \rangle = \sqrt{\frac{2}{5}}|m = 0, m_s = -\frac{1}{2} \rangle - \sqrt{\frac{3}{5}}|m = -1, m_s = \frac{1}{2} \rangle \\ |j = \frac{3}{2}, m_c = -\frac{3}{2} \rangle = \sqrt{\frac{1}{5}}|m = -1, m_s = -\frac{1}{2} \rangle - \sqrt{\frac{4}{5}}|m = -2, m_s = \frac{1}{2} \rangle \end{array} \right.$$