

课堂练习

练习1：证明如下结论：对于闭壳层行列式波函数，该行列式波函数一定是 \hat{S}^2 和 \hat{S}_z 的本征态，对应的自旋量子数 $S = 0$ ， $M_S = 0$ ；对于开壳层行列式波函数，如其中的所有单占据轨道（记其数目为 N_s ）电子具有相同自旋 α 或 β ，则该行列式波函数是 \hat{S}^2 和 \hat{S}_z 的本征态，对应的自旋量子数 $S = \frac{N_s}{2}$ ， $M_S = \frac{N_s}{2}$ 或 $-\frac{N_s}{2}$ （取决于单占据轨道电子向上或向下）

证明：首先证明行列式波函数是 \hat{S}_z 的本征态，由于 $\hat{S}_z = \sum_u \hat{s}_{z,u}$ ，因此设 $\chi_1, \chi_2, \dots, \chi_{N-N_s-1}, \chi_{N-N_s}$

为非单占轨道（ $N - N_s$ 为偶数），且 $\chi_{2i-1} = \psi_i \alpha$ ， $\chi_{2i} = \psi_i \beta$ ；而

$\chi_{N-N_s+1}, \chi_{N-N_s+2}, \dots, \chi_{N-1}, \chi_N$ 为单占轨道（特别的，若 $N_s = 0$ ，则无单占轨道），则

$$\begin{aligned} \hat{S}_z |\chi_1 \chi_2 \dots \chi_N\rangle &= \sum_{u=1}^N \hat{s}_{z,u} \cdot \frac{1}{\sqrt{N!}} \sum_P (-1)^P \chi_{P_1}(\mathbf{x}_1) \chi_{P_2}(\mathbf{x}_2) \dots \chi_{P_N}(\mathbf{x}_N) \\ &= \frac{1}{\sqrt{N!}} \sum_P (-1)^P \sum_{u=1}^N \chi_{P_1}(\mathbf{x}_1) \chi_{P_2}(\mathbf{x}_2) \dots [\hat{s}_{z,u} \chi_{P_u}(\mathbf{x}_u)] \dots \chi_{P_N}(\mathbf{x}_N) \\ &= \frac{1}{\sqrt{N!}} \sum_P (-1)^P \sum_{u=1}^N m_{s,u} \hbar \chi_{P_1}(\mathbf{x}_1) \chi_{P_2}(\mathbf{x}_2) \dots \chi_{P_u}(\mathbf{x}_u) \dots \chi_{P_N}(\mathbf{x}_N) \\ &= \frac{(N_\alpha - N_\beta) \hbar}{2\sqrt{N!}} \sum_P (-1)^P \chi_{P_1}(\mathbf{x}_1) \chi_{P_2}(\mathbf{x}_2) \dots \chi_{P_N}(\mathbf{x}_N) = \frac{1}{2} (N_\alpha - N_\beta) \hbar |\chi_1 \chi_2 \dots \chi_N\rangle \end{aligned}$$

若为闭壳层行列式波函数，则 $\hat{S}_z |\chi_1 \chi_2 \dots \chi_N\rangle = 0$ ， $M_S = 0$ ；若单占据轨道全部取自旋向上，则

$\hat{S}_z |\chi_1 \chi_2 \dots \chi_N\rangle = \frac{N_s}{2} \hbar |\chi_1 \chi_2 \dots \chi_N\rangle$ ， $M_S = \frac{N_s}{2}$ ；若单占据轨道全部取自旋向下，则

$\hat{S}_z |\chi_1 \chi_2 \dots \chi_N\rangle = -\frac{N_s}{2} \hbar |\chi_1 \chi_2 \dots \chi_N\rangle$ ， $M_S = -\frac{N_s}{2}$

接下来我们分析 \hat{S}^2 ，由于 $\hat{S}^2 = \hat{S}_+ \hat{S}_- - \hbar \hat{S}_z + \hat{S}_z^2$ ，而 $\hat{S}_+ = \sum_u \hat{s}_{u,+}$ ， $\hat{S}_- = \sum_u \hat{s}_{u,-}$ ，因此重点

在于分析 $\hat{S}_+ \hat{S}_-$ 的作用结果。若为闭壳层行列式波函数，则

$$\hat{S}_+ \hat{S}_- |\chi_1 \chi_2 \dots \chi_N\rangle = \hat{S}_+ (\hat{S}_- |\chi_1 \chi_2 \dots \chi_N\rangle) =$$

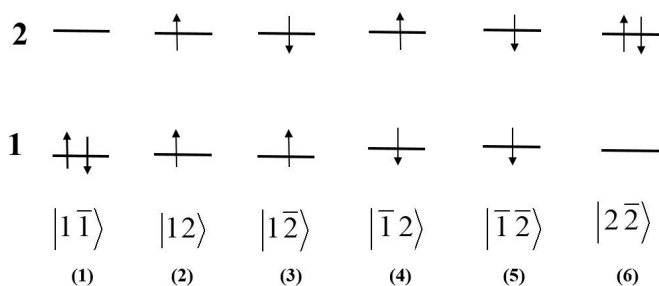
若单占据轨道全部取自旋向上，则：

$$< \text{Empty Math Block} >$$

若单占据轨道全部取自旋向下，则：

$$< \text{Empty Math Block} >$$

练习2：写出下图电子构型的哈密顿算符的期望值



解：图（1）构型的哈密尔顿算符的期望值为 $\langle 1\bar{1}|\hat{H}|1\bar{1}\rangle = 2h_{11} + J_{11}$

图（2）构型的哈密尔顿算符的期望值为 $\langle 12|\hat{H}|12\rangle = h_{11} + h_{22} + J_{12} - K_{12}$

图（3）构型的哈密尔顿算符的期望值为 $\langle 1\bar{2}|\hat{H}|1\bar{2}\rangle = h_{11} + h_{22} + J_{12}$

图（4）构型的哈密尔顿算符的期望值为 $\langle \bar{1}2|\hat{H}|\bar{1}2\rangle = h_{11} + h_{22} + J_{12}$

图（5）构型的哈密尔顿算符的期望值为 $\langle \bar{1}\bar{2}|\hat{H}|\bar{1}\bar{2}\rangle = h_{11} + h_{22} + J_{12} - K_{12}$

图（6）构型的哈密尔顿算符的期望值为 $\langle 2\bar{2}|\hat{H}|2\bar{2}\rangle = 2h_{22} + J_{22}$

练习3：证明 $\Theta_1(1, 2) = 2^{-\frac{1}{2}} [\alpha(1)\beta(2) - \alpha(2)\beta(1)] = \Theta_{0,0}(1, 2)$ **是量子数为** $(0, 0)$ **的自旋本征态，** $\Theta_2(1, 2) = 2^{-\frac{1}{2}} [\alpha(1)\beta(2) + \alpha(2)\beta(1)] = \Theta_{1,0}(1, 2)$ **是量子数为** $(1, 0)$ **的自旋本征态**

证明：由于

$$\hat{S}^2 = (\hat{s}_1 + \hat{s}_2)^2 = \hat{s}_1^2 + \hat{s}_2^2 + 2\hat{s}_1 \cdot \hat{s}_2 = \hat{s}_1^2 + \hat{s}_2^2 + 2(\hat{s}_{1,x}\hat{s}_{2,x} + \hat{s}_{1,y}\hat{s}_{2,y} + \hat{s}_{1,z}\hat{s}_{2,z})$$

故有

$$\begin{aligned} \hat{S}^2[\alpha(1)\beta(2)] &= [\hat{s}_1^2 + \hat{s}_2^2 + 2(\hat{s}_{1,x}\hat{s}_{2,x} + \hat{s}_{1,y}\hat{s}_{2,y} + \hat{s}_{1,z}\hat{s}_{2,z})][\alpha(1)\beta(2)] \\ &= [\hat{s}_1^2 + \hat{s}_2^2 + 2 \cdot \frac{1}{2}(\hat{s}_{1,+} + \hat{s}_{1,-}) \cdot \frac{1}{2}(\hat{s}_{2,+} + \hat{s}_{2,-}) + 2 \cdot \frac{1}{2i}(\hat{s}_{1,+} - \hat{s}_{1,-}) \cdot \frac{1}{2i}(\hat{s}_{2,+} - \hat{s}_{2,-}) + 2\hat{s}_{1,z}\hat{s}_{2,z}][\alpha(1)\beta(2)] \\ &= (\hat{s}_1^2 + \hat{s}_2^2)[\alpha(1)\beta(2)] + [\frac{1}{2}(\hat{s}_{1,+} + \hat{s}_{1,-})\alpha(1) \cdot (\hat{s}_{2,+} + \hat{s}_{2,-})\beta(2) - \frac{1}{2}(\hat{s}_{1,+} - \hat{s}_{1,-})\alpha(1) \cdot (\hat{s}_{2,+} - \hat{s}_{2,-})\beta(2) + 2\hat{s}_{1,z}\alpha(1) \cdot \hat{s}_{2,z}\beta(2)] \\ &= [\frac{1}{2}(\frac{1}{2} + 1)\hbar^2 + \frac{1}{2}(\frac{1}{2} + 1)\hbar^2][\alpha(1)\beta(2)] + [\frac{1}{2} \cdot \hbar\beta(1) \cdot \hbar\alpha(2) - \frac{1}{2} \cdot (-\hbar\beta(1)) \cdot \hbar\alpha(2) + 2 \cdot \frac{1}{2}\hbar \cdot (-\frac{1}{2}\hbar)\alpha(1)\beta(2)] \\ &= \hbar^2[\alpha(1)\beta(2) + \beta(1)\alpha(2)] \end{aligned}$$

$$\begin{aligned} \hat{S}^2[\alpha(2)\beta(1)] &= [\hat{s}_1^2 + \hat{s}_2^2 + 2(\hat{s}_{1,x}\hat{s}_{2,x} + \hat{s}_{1,y}\hat{s}_{2,y} + \hat{s}_{1,z}\hat{s}_{2,z})][\alpha(2)\beta(1)] \\ &= [\hat{s}_1^2 + \hat{s}_2^2 + 2 \cdot \frac{1}{2}(\hat{s}_{1,+} + \hat{s}_{1,-}) \cdot \frac{1}{2}(\hat{s}_{2,+} + \hat{s}_{2,-}) + 2 \cdot \frac{1}{2i}(\hat{s}_{1,+} - \hat{s}_{1,-}) \cdot \frac{1}{2i}(\hat{s}_{2,+} - \hat{s}_{2,-}) + 2\hat{s}_{1,z}\hat{s}_{2,z}][\alpha(2)\beta(1)] \\ &= (\hat{s}_1^2 + \hat{s}_2^2)[\alpha(2)\beta(1)] + [\frac{1}{2}(\hat{s}_{1,+} + \hat{s}_{1,-})\beta(1) \cdot (\hat{s}_{2,+} + \hat{s}_{2,-})\alpha(2) - \frac{1}{2}(\hat{s}_{1,+} - \hat{s}_{1,-})\beta(1) \cdot (\hat{s}_{2,+} - \hat{s}_{2,-})\alpha(2) + 2\hat{s}_{1,z}\beta(1) \cdot \hat{s}_{2,z}\alpha(2)] \\ &= [\frac{1}{2}(\frac{1}{2} + 1)\hbar^2 + \frac{1}{2}(\frac{1}{2} + 1)\hbar^2][\alpha(2)\beta(1)] + [\frac{1}{2} \cdot \hbar\alpha(1) \cdot \hbar\beta(2) - \frac{1}{2} \cdot \hbar\alpha(1) \cdot (-\hbar\beta(2)) + 2 \cdot (-\frac{1}{2})\hbar \cdot \frac{1}{2}\hbar\beta(1)\alpha(2)] \\ &= \hbar^2[\beta(1)\alpha(2) + \alpha(1)\beta(2)] \end{aligned}$$

从而

$$\begin{aligned} \hat{S}^2\Theta_1(1, 2) &= 2^{-\frac{1}{2}} \{\hat{S}^2[\alpha(1)\beta(2)] - \hat{S}^2[\alpha(2)\beta(1)]\} = 2^{-\frac{1}{2}} \{\hbar^2[\alpha(1)\beta(2) + \beta(1)\alpha(2)] - \hbar^2[\beta(1)\alpha(2) + \alpha(1)\beta(2)]\} \\ &= 0 = 0 \cdot (0 + 1)\hbar^2 \cdot \Theta_1(1, 2) \end{aligned}$$

$$\begin{aligned} \hat{S}_z\Theta_1(1, 2) &= 2^{-\frac{1}{2}} \{\hat{S}_z[\alpha(1)\beta(2)] - \hat{S}_z[\alpha(2)\beta(1)]\} = 2^{-\frac{1}{2}} \{(\hat{s}_{z,1} + \hat{s}_{z,2})[\alpha(1)\beta(2)] - (\hat{s}_{z,1} + \hat{s}_{z,2})[\alpha(2)\beta(1)]\} \\ &= 2^{-\frac{1}{2}} \{\hat{s}_{z,1}[\alpha(1)\beta(2)] + \hat{s}_{z,2}[\alpha(1)\beta(2)] - \hat{s}_{z,1}[\alpha(2)\beta(1)] - \hat{s}_{z,2}[\alpha(2)\beta(1)]\} \\ &= 2^{-\frac{1}{2}} \{\frac{1}{2}\hbar\alpha(1)\beta(2) - \frac{1}{2}\hbar\alpha(1)\beta(2) - (-\frac{1}{2}\hbar)\alpha(2)\beta(1) - \frac{1}{2}\hbar\alpha(2)\beta(1)\} \\ &= 0 = 0\hbar \cdot \Theta_1(1, 2) \end{aligned}$$

因此 $\Theta_1(1, 2)$ 是量子数为 $(0, 0)$ 的自旋本征态。

同理

$$\begin{aligned} \hat{S}^2\Theta_2(1, 2) &= 2^{-\frac{1}{2}} \{\hat{S}^2[\alpha(1)\beta(2)] + \hat{S}^2[\alpha(2)\beta(1)]\} = 2^{-\frac{1}{2}} \{\hbar^2[\alpha(1)\beta(2) + \beta(1)\alpha(2)] + \hbar^2[\beta(1)\alpha(2) + \alpha(1)\beta(2)]\} \\ &= \sqrt{2}\hbar^2[\alpha(1)\beta(2) + \beta(1)\alpha(2)] = 2\hbar^2 \cdot \Theta_2(1, 2) = 1 \cdot (1 + 1)\hbar^2 \cdot \Theta_2(1, 2) \end{aligned}$$

$$\begin{aligned}
\hat{S}_z \Theta_2(1, 2) &= 2^{-\frac{1}{2}} \{ \hat{S}_z [\alpha(1)\beta(2)] + \hat{S}_z [\alpha(2)\beta(1)] \} = 2^{-\frac{1}{2}} \{ (\hat{s}_{z,1} + \hat{s}_{z,2}) [\alpha(1)\beta(2)] + (\hat{s}_{z,1} + \hat{s}_{z,2}) [\alpha(2)\beta(1)] \} \\
&= 2^{-\frac{1}{2}} \{ \hat{s}_{z,1} [\alpha(1)\beta(2)] + \hat{s}_{z,2} [\alpha(1)\beta(2)] + \hat{s}_{z,1} [\alpha(2)\beta(1)] + \hat{s}_{z,2} [\alpha(2)\beta(1)] \} \\
&= 2^{-\frac{1}{2}} \{ \frac{1}{2} \hbar \alpha(1)\beta(2) - \frac{1}{2} \hbar \alpha(1)\beta(2) - \frac{1}{2} \hbar \alpha(2)\beta(1) + \frac{1}{2} \hbar \alpha(2)\beta(1) \} \\
&= 0 = 0\hbar \cdot \Theta_2(1, 2)
\end{aligned}$$

因此 $\Theta_2(1, 2)$ 是量子数为 $(1, 0)$ 的自旋本征态。

另证：由于 $\hat{S}^2 = \hat{S}_+ \hat{S}_- - \hbar \hat{S}_z + \hat{S}_z^2$ ，而 $\hat{S}_+ = \hat{s}_{1,+} + \hat{s}_{2,+}$ ， $\hat{S}_- = \hat{s}_{1,-} + \hat{s}_{2,-}$ ， $\hat{S}_z = \hat{s}_{z,1} + \hat{s}_{z,2}$ ，因此

$$\begin{aligned}
\hat{S}_z \Theta_1(1, 2) &= (\hat{s}_{z,1} + \hat{s}_{z,2}) \Theta_1(1, 2) = 2^{-\frac{1}{2}} \{ [\hat{s}_{z,1} \alpha(1)] \beta(2) - \alpha(2) [\hat{s}_{z,1} \beta(1)] + \alpha(1) [\hat{s}_{z,2} \beta(2)] - [\hat{s}_{z,2} \alpha(2)] \beta(1) \} \\
&= 2^{-\frac{1}{2}} \{ \frac{1}{2} \hbar \alpha(1)\beta(2) - (-\frac{1}{2} \hbar) \alpha(2)\beta(1) + (-\frac{1}{2} \hbar) \alpha(1)\beta(2) - \frac{1}{2} \hbar \alpha(2)\beta(1) \} = 0 = 0\hbar \cdot \Theta_1(1, 2)
\end{aligned}$$

$$\hat{S}_z^2 \Theta_1(1, 2) = \hat{S}_z (\hat{S}_z \Theta_1(1, 2)) = \hat{S}_z (0 \cdot \Theta_1(1, 2)) = 0 \cdot \hat{S}_z \Theta_1(1, 2) = 0$$

$$\begin{aligned}
\hat{S}_+ \hat{S}_- \Theta_1(1, 2) &= (\hat{s}_{1,+} + \hat{s}_{2,+})(\hat{s}_{1,-} + \hat{s}_{2,-}) \Theta_1(1, 2) = (\hat{s}_{1,+} + \hat{s}_{2,+})[(\hat{s}_{1,-} + \hat{s}_{2,-}) \Theta_1(1, 2)] \\
&= (\hat{s}_{1,+} + \hat{s}_{2,+}) \cdot 2^{-\frac{1}{2}} \{ [\hat{s}_{1,-} \alpha(1)] \beta(2) - \alpha(2) [\hat{s}_{1,-} \beta(1)] + \alpha(1) [\hat{s}_{2,-} \beta(2)] - [\hat{s}_{2,-} \alpha(2)] \beta(1) \} \\
&= (\hat{s}_{1,+} + \hat{s}_{2,+}) \cdot 2^{-\frac{1}{2}} \{ \hbar \beta(1) \cdot \beta(2) - \alpha(2) \cdot 0 + \alpha(1) \cdot 0 - \hbar \beta(2) \cdot \beta(1) \} = 0
\end{aligned}$$

从而

$$\hat{S}^2 \Theta_1(1, 2) = (\hat{S}_+ \hat{S}_- - \hbar \hat{S}_z + \hat{S}_z^2) \Theta_1(1, 2) = \hat{S}_+ \hat{S}_- \Theta_1(1, 2) - \hbar \hat{S}_z \Theta_1(1, 2) + \hat{S}_z^2 \Theta_1(1, 2) = 0 = 0 \cdot (0+1) \hbar^2 \Theta_1(1, 2)$$

即 $\Theta_1(1, 2)$ 是量子数为 $(0, 0)$ 的自旋本征态。

同理可得

$$\begin{aligned}
\hat{S}_z \Theta_2(1, 2) &= (\hat{s}_{z,1} + \hat{s}_{z,2}) \Theta_2(1, 2) = 2^{-\frac{1}{2}} \{ [\hat{s}_{z,1} \alpha(1)] \beta(2) + \alpha(2) [\hat{s}_{z,1} \beta(1)] + \alpha(1) [\hat{s}_{z,2} \beta(2)] + [\hat{s}_{z,2} \alpha(2)] \beta(1) \} \\
&= 2^{-\frac{1}{2}} \{ \frac{1}{2} \hbar \alpha(1)\beta(2) + (-\frac{1}{2} \hbar) \alpha(2)\beta(1) + (-\frac{1}{2} \hbar) \alpha(1)\beta(2) + \frac{1}{2} \hbar \alpha(2)\beta(1) \} = 0 = 0\hbar \cdot \Theta_2(1, 2)
\end{aligned}$$

$$\hat{S}_z^2 \Theta_2(1, 2) = \hat{S}_z (\hat{S}_z \Theta_2(1, 2)) = \hat{S}_z (0 \cdot \Theta_2(1, 2)) = 0 \cdot \hat{S}_z \Theta_2(1, 2) = 0$$

$$\begin{aligned}
\hat{S}_+ \hat{S}_- \Theta_2(1, 2) &= (\hat{s}_{1,+} + \hat{s}_{2,+})(\hat{s}_{1,-} + \hat{s}_{2,-}) \Theta_2(1, 2) = (\hat{s}_{1,+} + \hat{s}_{2,+})[(\hat{s}_{1,-} + \hat{s}_{2,-}) \Theta_2(1, 2)] \\
&= (\hat{s}_{1,+} + \hat{s}_{2,+}) \cdot 2^{-\frac{1}{2}} \{ [\hat{s}_{1,-} \alpha(1)] \beta(2) + \alpha(2) [\hat{s}_{1,-} \beta(1)] + \alpha(1) [\hat{s}_{2,-} \beta(2)] + [\hat{s}_{2,-} \alpha(2)] \beta(1) \} \\
&= (\hat{s}_{1,+} + \hat{s}_{2,+}) \cdot 2^{-\frac{1}{2}} \{ \hbar \beta(1) \cdot \beta(2) + \alpha(2) \cdot 0 + \alpha(1) \cdot 0 + \hbar \beta(2) \cdot \beta(1) \} = (\hat{s}_{1,+} + \hat{s}_{2,+}) [\sqrt{2} \hbar \beta(1)\beta(2)] \\
&= \sqrt{2} \hbar \{ [\hat{s}_{1,+} \beta(1)] \beta(2) + \beta(1) [\hat{s}_{2,+} \beta(2)] \} = \sqrt{2} \hbar \{ \hbar \alpha(1) \cdot \beta(2) + \beta(1) \cdot \hbar \alpha(2) \} \\
&= \sqrt{2} \hbar^2 \{ \alpha(1)\beta(2) + \beta(1)\alpha(2) \} = 2\hbar^2 \Theta_2(1, 2) = 1 \cdot (1+1) \hbar^2 \Theta_2(1, 2)
\end{aligned}$$

从而

$$\hat{S}^2 \Theta_2(1, 2) = (\hat{S}_+ \hat{S}_- - \hbar \hat{S}_z + \hat{S}_z^2) \Theta_2(1, 2) = \hat{S}_+ \hat{S}_- \Theta_2(1, 2) - \hbar \hat{S}_z \Theta_2(1, 2) + \hat{S}_z^2 \Theta_2(1, 2) = 1 \cdot (1+1) \hbar^2 \Theta_2(1, 2)$$

即 $\Theta_2(1, 2)$ 是量子数为 $(1, 0)$ 的自旋本征态。

习题3.3

$$1. \text{证明自旋污染的表达式 } \langle \hat{S}^2 \rangle_{\text{UHF}} = \langle \hat{S}^2 \rangle_{\text{exact}} + N_\beta - \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\beta} |S_{ij}^{\alpha\beta}|^2$$

证明：

$$2. \text{考虑一个两电子体系的UHF波函数 } |K\rangle = |\psi_1^\alpha \bar{\psi}_1^\beta\rangle, \text{ 推导 } \langle K | \hat{S}^2 | K \rangle \text{ 的表达式}$$

解：由于

$$\begin{aligned}
|K\rangle &= \frac{1}{\sqrt{2!}} \begin{vmatrix} \psi_1^\alpha(\mathbf{x}_1) & \bar{\psi}_1^\beta(\mathbf{x}_1) \\ \psi_1^\alpha(\mathbf{x}_2) & \bar{\psi}_1^\beta(\mathbf{x}_2) \end{vmatrix} = \frac{1}{\sqrt{2!}} [\psi_1^\alpha(\mathbf{x}_1)\bar{\psi}_1^\beta(\mathbf{x}_2) - \bar{\psi}_1^\beta(\mathbf{x}_1)\psi_1^\alpha(\mathbf{x}_2)] \\
&= \frac{1}{\sqrt{2!}} [\psi_1^\alpha(\mathbf{r}_1)\alpha(s_1)\psi_1^\beta(\mathbf{r}_2)\beta(s_2) - \psi_1^\beta(\mathbf{r}_1)\beta(s_1)\psi_1^\alpha(\mathbf{r}_2)\alpha(s_2)]
\end{aligned}$$

结合练习2的推论 $\hat{S}^2[\alpha(s_1)\beta(s_2)] = \hbar^2[\alpha(s_1)\beta(s_2) + \beta(s_1)\alpha(s_2)]$,
 $\hat{S}^2[\alpha(s_2)\beta(s_1)] = \hbar^2[\alpha(s_1)\beta(s_2) + \beta(s_1)\alpha(s_2)]$, 得:

$$\begin{aligned}
\hat{S}^2|K\rangle &= \frac{1}{\sqrt{2!}} \{ \psi_1^\alpha(\mathbf{r}_1)\psi_1^\beta(\mathbf{r}_2)\hat{S}^2[\alpha(s_1)\beta(s_2)] - \psi_1^\beta(\mathbf{r}_1)\psi_1^\alpha(\mathbf{r}_2)\hat{S}^2[\beta(s_1)\alpha(s_2)] \} \\
&= \frac{\hbar^2}{\sqrt{2!}} [\psi_1^\alpha(\mathbf{r}_1)\psi_1^\beta(\mathbf{r}_2) - \psi_1^\beta(\mathbf{r}_1)\psi_1^\alpha(\mathbf{r}_2)] [\alpha(s_1)\beta(s_2) + \beta(s_1)\alpha(s_2)] \\
&= \frac{\hbar^2}{\sqrt{2!}} |K\rangle + \frac{\hbar^2}{\sqrt{2!}} [\psi_1^\alpha(\mathbf{r}_1)\beta(s_1)\psi_1^\beta(\mathbf{r}_2)\alpha(s_2) - \psi_1^\beta(\mathbf{r}_1)\alpha(s_1)\psi_1^\alpha(\mathbf{r}_2)\beta(s_2)]
\end{aligned}$$

因此

$$\begin{aligned}
\langle K|\hat{S}^2|K\rangle &= \frac{\hbar^2}{2!} \langle K|K\rangle + \frac{\hbar^2}{2!} \iiint \begin{vmatrix} \psi_1^{\alpha*}(\mathbf{r}_1)\alpha^*(s_1) & \psi_1^{\beta*}(\mathbf{r}_1)\beta^*(s_1) \\ \psi_1^{\alpha*}(\mathbf{r}_2)\alpha^*(s_2) & \psi_1^{\beta*}(\mathbf{r}_2)\beta^*(s_2) \end{vmatrix} \begin{vmatrix} \psi_1^\alpha(\mathbf{r}_1)\beta(s_1) & \psi_1^\beta(\mathbf{r}_1)\alpha(s_1) \\ \psi_1^\alpha(\mathbf{r}_2)\beta(s_2) & \psi_1^\beta(\mathbf{r}_2)\alpha(s_2) \end{vmatrix} d\mathbf{r}_1 d\mathbf{r}_2 ds_1 ds_2 \\
&= \hbar^2 + \frac{\hbar^2}{2!} \iiint [|\psi_1^\alpha(\mathbf{r}_1)|^2 |\psi_1^\beta(\mathbf{r}_2)|^2 \alpha^*(s_1)\beta(s_1)\beta^*(s_2)\alpha(s_2) - \psi_1^{\alpha*}(\mathbf{r}_1)\psi_1^\beta(\mathbf{r}_1)\psi_1^{\beta*}(\mathbf{r}_2)\psi_1^\alpha(\mathbf{r}_2) |\alpha(s_1)|^2 |\beta(s_2)|^2] d\mathbf{r}_1 d\mathbf{r}_2 ds_1 ds_2 \\
&\quad + \frac{\hbar^2}{2!} \iiint [|\psi_1^\beta(\mathbf{r}_1)|^2 |\psi_1^\alpha(\mathbf{r}_2)|^2 \beta^*(s_1)\alpha(s_1)\alpha^*(s_2)\beta(s_2) - \psi_1^{\beta*}(\mathbf{r}_1)\psi_1^\alpha(\mathbf{r}_1)\psi_1^{\alpha*}(\mathbf{r}_2)\psi_1^\beta(\mathbf{r}_2) |\beta(s_1)|^2 |\alpha(s_2)|^2] d\mathbf{r}_1 d\mathbf{r}_2 ds_1 ds_2 \\
&= \hbar^2 - \frac{\hbar^2}{2} \int \psi_1^{\alpha*}(\mathbf{r}_1)\psi_1^\beta(\mathbf{r}_1) d\mathbf{r}_1 \int \psi_1^{\beta*}(\mathbf{r}_2)\psi_1^\alpha(\mathbf{r}_2) d\mathbf{r}_2 - \frac{\hbar^2}{2} \int \psi_1^{\beta*}(\mathbf{r}_1)\psi_1^\alpha(\mathbf{r}_1) d\mathbf{r}_1 \int \psi_1^{\alpha*}(\mathbf{r}_2)\psi_1^\beta(\mathbf{r}_2) d\mathbf{r}_2 \\
&= \frac{\hbar^2}{2} (2 - S_{11}^{\alpha\beta} S_{11}^{\beta\alpha} - S_{11}^{\beta\alpha} S_{11}^{\alpha\beta}) = \hbar^2 (1 - |S_{11}^{\alpha\beta}|^2)
\end{aligned}$$

若采用原子单位制, 则 $\langle K|\hat{S}^2|K\rangle = 1 - |S_{11}^{\alpha\beta}|^2$

课堂练习 (续)

练习3: 证明 $i \neq j$ 时, 有 $\{\hat{a}_i, \hat{a}_j^\dagger\} = 0$

证明: 设已有Slater行列式波函数 $|\psi_1 \psi_2 \dots \psi_N\rangle$, 则当 $i \notin \{1, 2, \dots, N\}$, $j \notin \{1, 2, \dots, N\}$ 时, 根据产生和湮灭算符的定义, 有:

$$\begin{aligned}
\{\hat{a}_i, \hat{a}_j^\dagger\} |\psi_1 \psi_2 \dots \psi_N\rangle &= (\hat{a}_i \hat{a}_j^\dagger + \hat{a}_j^\dagger \hat{a}_i) |\psi_1 \psi_2 \dots \psi_N\rangle = \hat{a}_i \hat{a}_j^\dagger |\psi_1 \psi_2 \dots \psi_N\rangle + \hat{a}_j^\dagger \hat{a}_i |\psi_1 \psi_2 \dots \psi_N\rangle \\
&= \hat{a}_i |\psi_1 \psi_2 \dots \psi_N \psi_j\rangle + \hat{a}_j^\dagger \cdot 0 = 0
\end{aligned}$$

当 $i \notin \{1, 2, \dots, N\}$, $j \in \{1, 2, \dots, N\}$ 时, 有:

$$\begin{aligned}
\{\hat{a}_i, \hat{a}_j^\dagger\} |\psi_1 \psi_2 \dots \psi_N\rangle &= (\hat{a}_i \hat{a}_j^\dagger + \hat{a}_j^\dagger \hat{a}_i) |\psi_1 \psi_2 \dots \psi_N\rangle = \hat{a}_i \hat{a}_j^\dagger |\psi_1 \psi_2 \dots \psi_N\rangle + \hat{a}_j^\dagger \hat{a}_i |\psi_1 \psi_2 \dots \psi_N\rangle \\
&= \hat{a}_i \cdot 0 + \hat{a}_j^\dagger \cdot 0 = 0
\end{aligned}$$

当 $i \in \{1, 2, \dots, N\}$, $j \notin \{1, 2, \dots, N\}$ 时, 记第 i 个波函数被湮灭后, Slater行列式波函数变为 $|\psi_1 \psi_2 \dots 0_i \dots \psi_N\rangle = (-1)^P |\psi_1 \psi_2 \dots \psi_N 0_i\rangle = (-1)^P |\psi_1 \psi_2 \dots \psi_N\rangle$, 则:

$$\begin{aligned}
\{\hat{a}_i, \hat{a}_j^\dagger\} |\psi_1 \psi_2 \dots \psi_N\rangle &= (\hat{a}_i \hat{a}_j^\dagger + \hat{a}_j^\dagger \hat{a}_i) |\psi_1 \psi_2 \dots \psi_N\rangle = \hat{a}_i \hat{a}_j^\dagger |\psi_1 \psi_2 \dots \psi_N\rangle + \hat{a}_j^\dagger \hat{a}_i |\psi_1 \psi_2 \dots \psi_N\rangle \\
&= \hat{a}_i |\psi_1 \psi_2 \dots \psi_N \psi_j\rangle + \hat{a}_j^\dagger |\psi_1 \psi_2 \dots 0_i \dots \psi_N\rangle \\
&= |\psi_1 \psi_2 \dots 0_i \dots \psi_N \psi_j\rangle + (-1)^P \hat{a}_j^\dagger |\psi_1 \psi_2 \dots \psi_N 0_i\rangle \\
&= (-1)^{P'} |\psi_1 \psi_2 \dots \psi_N \psi_j 0_i\rangle + (-1)^P |\psi_1 \psi_2 \dots \psi_N 0_i \psi_j\rangle
\end{aligned}$$

由于 $|\psi_1 \psi_2 \dots 0_i \dots \psi_N \psi_j\rangle \xrightarrow{\text{operation } P} |\psi_1 \psi_2 \dots \psi_N 0_i \psi_j\rangle \xrightarrow{\text{swap } \psi_j \text{ and } 0_i} |\psi_1 \psi_2 \dots \psi_N \psi_j 0_i\rangle$, 因此 $P' = P + 1$, 从而有:

$$\{\hat{a}_i, \hat{a}_j^\dagger\} |\psi_1 \psi_2 \dots \psi_N\rangle = -(-1)^P |\psi_1 \psi_2 \dots \psi_N \psi_j\rangle + (-1)^P |\psi_1 \psi_2 \dots \psi_N \psi_j\rangle = 0$$

当 $i \in \{1, 2, \dots, N\}$, $j \in \{1, 2, \dots, N\}$ 时, 有:

$$\begin{aligned} \{\hat{a}_i, \hat{a}_j^\dagger\} |\psi_1 \psi_2 \dots \psi_N\rangle &= (\hat{a}_i \hat{a}_j^\dagger + \hat{a}_j^\dagger \hat{a}_i) |\psi_1 \psi_2 \dots \psi_N\rangle = \hat{a}_i \hat{a}_j^\dagger |\psi_1 \psi_2 \dots \psi_N\rangle + \hat{a}_j^\dagger \hat{a}_i |\psi_1 \psi_2 \dots \psi_N\rangle \\ &= \hat{a}_i \cdot 0 + \hat{a}_j^\dagger |\psi_1 \psi_2 \dots 0_i \dots \psi_N\rangle = (-1)^P \hat{a}_j^\dagger |\psi_1 \psi_2 \dots \psi_N 0_i\rangle = 0 \end{aligned}$$

练习4: 根据从占据数矢量出发的产生和湮灭算符的定义, 推导产生湮灭算符之间的反对易关系

证明: 采用占据数矢量, 产生和湮灭算符可以定义为

$$\begin{aligned} \hat{a}_i^\dagger |k_1 k_2 \dots k_{i-1} k_i k_{i+1} \dots k_M\rangle &= \delta_{k_i, 0} \prod_{j=i+1}^M (-1)^{k_j} |k_1 k_2 \dots k_{i-1} 1_i k_{i+1} \dots k_M\rangle \\ \hat{a}_i |k_1 k_2 \dots k_{i-1} k_i k_{i+1} \dots k_M\rangle &= \delta_{k_i, 1} \prod_{j=i+1}^M (-1)^{k_j} |k_1 k_2 \dots k_{i-1} 0_i k_{i+1} \dots k_M\rangle \end{aligned}$$

若 $i = j$, 则由于 $\{\hat{a}_i, \hat{a}_i^\dagger\} = \hat{a}_i \hat{a}_i^\dagger + \hat{a}_i^\dagger \hat{a}_i$, 而

$$\begin{aligned} \hat{a}_i \hat{a}_i^\dagger |k_1 k_2 \dots k_{i-1} k_i k_{i+1} \dots k_M\rangle &= \hat{a}_i \delta_{k_i, 0} \prod_{j=i+1}^M (-1)^{k_j} |k_1 k_2 \dots k_{i-1} 1_i k_{i+1} \dots k_M\rangle \\ &= \delta_{k_i, 0} \prod_{j'=i+1}^M (-1)^{k'_j} \prod_{j=i+1}^M (-1)^{k_j} |k_1 k_2 \dots k_{i-1} 0_i k_{i+1} \dots k_M\rangle \\ \hat{a}_i^\dagger \hat{a}_i |k_1 k_2 \dots k_{i-1} k_i k_{i+1} \dots k_M\rangle &= \hat{a}_i^\dagger \delta_{k_i, 1} \prod_{j=i+1}^M (-1)^{k_j} |k_1 k_2 \dots k_{i-1} 0_i k_{i+1} \dots k_M\rangle \\ &= \delta_{k_i, 1} \prod_{j'=i+1}^M (-1)^{k'_j} \prod_{j=i+1}^M (-1)^{k_j} |k_1 k_2 \dots k_{i-1} 1_i k_{i+1} \dots k_M\rangle \end{aligned}$$

因此

$$\begin{aligned} \{\hat{a}_i, \hat{a}_i^\dagger\} |k_1 k_2 \dots k_{i-1} k_i k_{i+1} \dots k_M\rangle &= \delta_{k_i, 0} \prod_{j'=i+1}^M (-1)^{k'_j} \prod_{j=i+1}^M (-1)^{k_j} |k_1 k_2 \dots k_{i-1} 0_i k_{i+1} \dots k_M\rangle \\ &\quad + \delta_{k_i, 1} \prod_{j'=i+1}^M (-1)^{k'_j} \prod_{j=i+1}^M (-1)^{k_j} |k_1 k_2 \dots k_{i-1} 1_i k_{i+1} \dots k_M\rangle \\ &= \delta_{k_i, 0} |k_1 k_2 \dots k_{i-1} 0_i k_{i+1} \dots k_M\rangle + \delta_{k_i, 1} |k_1 k_2 \dots k_{i-1} 1_i k_{i+1} \dots k_M\rangle \end{aligned}$$

从而有 $\{\hat{a}_i, \hat{a}_i^\dagger\} = 1$

若 $i \neq j$, 不妨设 $i < j$ ($i > j$ 同理), 则由于 $\{\hat{a}_i, \hat{a}_j^\dagger\} = \hat{a}_i \hat{a}_j^\dagger + \hat{a}_j^\dagger \hat{a}_i$, 而

$$\begin{aligned} \hat{a}_i \hat{a}_j^\dagger |k_1 k_2 \dots k_i \dots k_j \dots k_M\rangle &= \hat{a}_i \delta_{k_j, 0} \prod_{l=j+1}^M (-1)^{k_l} |k_1 k_2 \dots k_i \dots 1_j \dots k_M\rangle \\ &= \delta_{k_i, 1} \delta_{k_j, 0} \prod_{l'=i+1}^M (-1)^{k'_{l'}} \prod_{l=j+1}^M (-1)^{k_l} |k_1 k_2 \dots 0_i \dots 1_j \dots k_M\rangle \end{aligned}$$

$$\begin{aligned}
\hat{a}_j^\dagger \hat{a}_i |k_1 k_2 \dots k_i \dots k_j \dots k_M\rangle &= \hat{a}_j^\dagger \delta_{k_i,1} \prod_{l=i+1}^M (-1)^{k_l} |k_1 k_2 \dots 0_i \dots k_j \dots k_M\rangle \\
&= \delta_{k_j,0} \delta_{k_i,1} \prod_{l'=j+1}^M (-1)^{k_{l'}} \prod_{l=i+1}^M (-1)^{k_l} |k_1 k_2 \dots 0_i \dots 1_j \dots k_M\rangle
\end{aligned}$$

因此

$$\begin{aligned}
\{\hat{a}_i, \hat{a}_j^\dagger\} |k_1 k_2 \dots k_i \dots k_j \dots k_M\rangle &= \delta_{k_i,1} \delta_{k_j,0} \prod_{l'=i+1}^M (-1)^{k_{l'}} \prod_{l=j+1}^M (-1)^{k_l} |k_1 k_2 \dots 0_i \dots 1_j \dots k_M\rangle \\
&\quad + \delta_{k_j,0} \delta_{k_i,1} \prod_{l'=j+1}^M (-1)^{k_{l'}} \prod_{l=i+1}^M (-1)^{k_l} |k_1 k_2 \dots 0_i \dots 1_j \dots k_M\rangle \\
&= \delta_{k_i,1} \delta_{k_j,0} \cdot (-1)^{\sum_{l'=i+1}^{j-1} k_{l'} + \sum_{l'=j+1}^M k_{l'} + 1} \cdot (-1)^{\sum_{l=j+1}^M k_l} |k_1 k_2 \dots 0_i \dots 1_j \dots k_M\rangle \\
&\quad + \delta_{k_j,0} \delta_{k_i,1} \cdot (-1)^{\sum_{l'=j+1}^M k_{l'}} \cdot (-1)^{\sum_{l=i+1}^{j-1} k_l + \sum_{l=j+1}^M k_l + k_j} |k_1 k_2 \dots 0_i \dots 1_j \dots k_M\rangle
\end{aligned}$$

由上式可知，当且仅当 $\begin{cases} k_j = 0 \\ k_i = 1 \end{cases}$ 时， $\delta_{k_j,0} \delta_{k_i,1}$ 方能不为零，但此时第一项与第二项正好互为相反数，使得两项相互抵消，从而有 $\{\hat{a}_i, \hat{a}_j^\dagger\} = 0$

练习5：证明场算符满足如下对应关系： (1) $\{\hat{\psi}(x), \hat{\psi}(x')\} = 0$; (2) $\{\hat{\psi}^\dagger(x), \hat{\psi}^\dagger(x')\} = 0$; (3) $\{\hat{\psi}(x), \hat{\psi}^\dagger(x')\} = \delta(x - x')$

证明：