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$\hat{S}_z=\sum\limits_u \hat{s}_{z,u}$，因此设$\chi_1,\chi_2,\ldots,\chi_{N-N_s-1},\chi_{N-N_s}$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$\chi_{N-N_s+1},\chi_{N-N_s+2},\ldots,\chi_{N-1},\chi_N$为单占轨道（特别的，若$N_s=0$，则无单占轨道），则

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

若为闭壳层行列式波函数，则$\hat{S}_z|\chi_1\chi_2\ldots\chi_N\rangle=0$，$M_S=0$；若单占据轨道全部取自旋向上，则$\hat{S}_z|\chi_1\chi_2\ldots\chi_N\rangle=\frac{N_s}{2}\hbar|\chi_1\chi_2\ldots\chi_N\rangle$，$M_S=\frac{N_s}{2}$；若单占据轨道全部取自旋向下，则$\hat{S}_z|\chi_1\chi_2\ldots\chi_N\rangle=-\frac{N_s}{2}\hbar|\chi_1\chi_2\ldots\chi_N\rangle$，$M_S=-\frac{N_s}{2}$
接下来我们来分析$\hat{S}^2$，由于$\hat{S}^2=\hat{S}_+\hat{S}_--\hbar\hat{S}_z+\hat{S}_z^2$，而$\hat{S}_+=\sum\limits_u\hat{s}_{u,+}$，$\hat{S}_-=\sum\limits_u\hat{s}_{u,-}$，因此

$\hat{S}_+\hat{S}_-=\sum\limits_u\hat{s}_{u,+}\cdot\sum\limits_v\hat{s}_{v,-}=\sum\limits_u\hat{s}_{u,+}\hat{s}_{u,-}+\sum\limits_{u\neq v}\hat{s}_{u,+}\hat{s}_{v,-}$

若为闭壳层行列式波函数，则

$$\hat{S}_+\hat{S}_-|\chi_1\chi_2\ldots\chi_N\rangle=?$$

若单占据轨道全部取自旋向上，则：

$$< Empty\ Math\ Block >$$

若单占据轨道全部取自旋向下，则：

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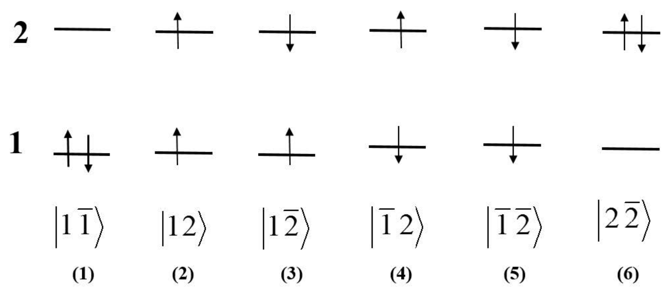
练习2：写出下图电子构型的哈密尔顿算符的期望值



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

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

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

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

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

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

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

从而

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

即$\Theta_2(1,2)$是量子数为$(1,0)$的自旋本征态。

习题3.3

1.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：易知$\hat{S}^2=\hat{S}_-\hat{S}_++\hbar\hat{S}_z+\hat{S}_z^2$，而$\hat{S}_z|\chi_1\chi_2\ldots\chi_N\rangle=\frac{1}{2}(N_\alpha-N_\beta)\hbar|\chi_1\chi_2\ldots\chi_N\rangle$，因此有

$$
\begin{aligned}
\langle\hat{S}^2\rangle_{\mathrm{UHF}} &= \langle\chi_1\chi_2\ldots\chi_N|\hat{S}^2|\chi_1\chi_2\ldots\chi_N\rangle = \langle\chi_1\chi_2\ldots\chi_N|\hat{S}_-\hat{S}_+ + \hbar\hat{S}_z + \hat{S}_z^2|\chi_1\chi_2\ldots\chi_N\rangle \\
&= \langle\chi_1\chi_2\ldots\chi_N|\hat{S}_-\hat{S}_+|\chi_1\chi_2\ldots\chi_N\rangle + \langle\chi_1\chi_2\ldots\chi_N|\hbar\hat{S}_z|\chi_1\chi_2\ldots\chi_N\rangle + \langle\chi_1\chi_2\ldots\chi_N|\hat{S}_z^2|\chi_1\chi_2\ldots\chi_N\rangle \\
&= \langle\chi_1\chi_2\ldots\chi_N|\hat{S}_-\hat{S}_+|\chi_1\chi_2\ldots\chi_N\rangle + \frac{N_\alpha - N_\beta}{2}(\frac{N_\alpha - N_\beta}{2} + 1)\hbar^2
\end{aligned}
$$

现在考虑$\hat{S}_-\hat{S}_+$的作用效果，显然$\hat{S}_+ = \sum\limits_u \hat{s}_{u,+}$，$\hat{S}_- = \sum\limits_u \hat{s}_{u,-}$，因此

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

解：由于

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

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：

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

因此

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

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$|\psi_1\psi_2\ldots\psi_N\rangle$，则当$i \notin \{1,2,\ldots,N\}$，$j \notin \{1,2,\ldots,N\}$时，根据产生和湮灭算符的定义，有：

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

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

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

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

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

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

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

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

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

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

$$
\begin{aligned}
\hat{a}_i^\dagger|k_1k_2\ldots k_{i-1}k_ik_{i+1}\ldots k_M\rangle &= \delta_{k_i,0}\prod_{j=i+1}^{M}(-1)^{k_j}|k_1k_2\ldots k_{i-1}1_ik_{i+1}\ldots k_M\rangle \\
\hat{a}_i|k_1k_2\ldots k_{i-1}k_ik_{i+1}\ldots k_M\rangle &= \delta_{k_i,1}\prod_{j=i+1}^{M}(-1)^{k_j}|k_1k_2\ldots k_{i-1}0_ik_{i+1}\ldots k_M\rangle
\end{aligned}
$$

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

$$
\begin{aligned}
\hat{a}_i\hat{a}_i^\dagger|k_1k_2\ldots k_{i-1}k_ik_{i+1}\ldots k_M\rangle &= \hat{a}_i\delta_{k_i,0}\prod_{j=i+1}^{M}(-1)^{k_j}|k_1k_2\ldots k_{i-1}1_ik_{i+1}\ldots k_M\rangle \\
&= \delta_{k_i,0}\prod_{j'=i+1}^{M}(-1)^{k_j'}\prod_{j=i+1}^{M}(-1)^{k_j}|k_1k_2\ldots k_{i-1}0_ik_{i+1}\ldots k_M\rangle
\end{aligned}
$$

$$
\begin{aligned}
\hat{a}_i^\dagger\hat{a}_i|k_1k_2\ldots k_{i-1}k_ik_{i+1}\ldots k_M\rangle &= \hat{a}_i^\dagger\delta_{k_i,1}\prod_{j=i+1}^{M}(-1)^{k_j}|k_1k_2\ldots k_{i-1}0_ik_{i+1}\ldots k_M\rangle \\
&= \delta_{k_i,1}\prod_{j'=i+1}^{M}(-1)^{k_j'}\prod_{j=i+1}^{M}(-1)^{k_j}|k_1k_2\ldots k_{i-1}1_ik_{i+1}\ldots k_M\rangle
\end{aligned}
$$

因此

$$
\begin{aligned}
\{\hat{a}_i,\hat{a}_i^\dagger\}|k_1k_2\ldots k_{i-1}k_ik_{i+1}\ldots k_M\rangle &= \delta_{k_i,0}\prod_{j'=i+1}^{M}(-1)^{k_j'}\prod_{j=i+1}^{M}(-1)^{k_j}|k_1k_2\ldots k_{i-1}0_ik_{i+1}\ldots k_M\rangle \\
&\quad+\delta_{k_i,1}\prod_{j'=i+1}^{M}(-1)^{k_j'}\prod_{j=i+1}^{M}(-1)^{k_j}|k_1k_2\ldots k_{i-1}1_ik_{i+1}\ldots k_M\rangle \\
&= \delta_{k_i,0}|k_1k_2\ldots k_{i-1}0_ik_{i+1}\ldots k_M\rangle+\delta_{k_i,1}|k_1k_2\ldots k_{i-1}1_ik_{i+1}\ldots k_M\rangle
\end{aligned}
$$

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

$$\begin{aligned}\hat{a}_i\hat{a}_j^\dagger|k_1k_2\ldots k_i\ldots k_j\ldots k_M\rangle&=\hat{a}_i\delta_{k_j,0}\prod_{l=j+1}^{M}(-1)^{k_l}|k_1k_2\ldots k_i\ldots 1_j\ldots k_M\rangle\\&=\delta_{k_i,1}\delta_{k_j,0}\prod_{l'=i+1}^{M}(-1)^{k_{l'}}\prod_{l=j+1}^{M}(-1)^{k_l}|k_1k_2\ldots 0_i\ldots 1_j\ldots k_M\rangle\end{aligned}$$

$$\begin{aligned}\hat{a}_j^\dagger\hat{a}_i|k_1k_2\ldots k_i\ldots k_j\ldots k_M\rangle&=\hat{a}_j^\dagger\delta_{k_i,1}\prod_{l=i+1}^{M}(-1)^{k_l}|k_1k_2\ldots 0_i\ldots k_j\ldots k_M\rangle\\&=\delta_{k_j,0}\delta_{k_i,1}\prod_{l'=j+1}^{M}(-1)^{k_{l'}}\prod_{l=i+1}^{M}(-1)^{k_l}|k_1k_2\ldots 0_i\ldots 1_j\ldots k_M\rangle\end{aligned}$$

因此

$$\begin{aligned}\{\hat{a}_i,\hat{a}_j^\dagger\}|k_1k_2\ldots k_i\ldots k_j\ldots k_M\rangle&=\delta_{k_i,1}\delta_{k_j,0}\prod_{l'=i+1}^{M}(-1)^{k_{l'}}\prod_{l=j+1}^{M}(-1)^{k_l}|k_1k_2\ldots 0_i\ldots 1_j\ldots k_M\rangle\\&\quad+\delta_{k_j,0}\delta_{k_i,1}\prod_{l'=j+1}^{M}(-1)^{k_{l'}}\prod_{l=i+1}^{M}(-1)^{k_l}|k_1k_2\ldots 0_i\ldots 1_j\ldots k_M\rangle\\&=\delta_{k_i,1}\delta_{k_j,0}\cdot(-1)^{\sum\limits_{l'=i+1}^{j-1}k_{l'}+\sum\limits_{l'=j+1}^{M}k_{l'}+1}\cdot(-1)^{\sum\limits_{l=j+1}^{M}k_l}|k_1k_2\ldots 0_i\ldots 1_j\ldots k_M\rangle\\&\quad+\delta_{k_j,0}\delta_{k_i,1}\cdot(-1)^{\sum\limits_{l'=j+1}^{M}k_{l'}}\cdot(-1)^{\sum\limits_{l=i+1}^{j-1}k_l+\sum\limits_{l=j+1}^{M}k_l+k_j}|k_1k_2\ldots 0_i\ldots 1_j\ldots k_M\rangle\end{aligned}$$

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）$\{\hat{\psi}(\boldsymbol{x}),\hat{\psi}(\boldsymbol{x}')\}=0$；（2）$\{\hat{\psi}^\dagger(\boldsymbol{x}),\hat{\psi}^\dagger(\boldsymbol{x}')\}=0$；（3）$\{\hat{\psi}(\boldsymbol{x}),\hat{\psi}^\dagger(\boldsymbol{x}')\}=\delta(\boldsymbol{x}-\boldsymbol{x}')$

证明：场算符的定义为$\begin{cases}\hat{\psi}(\boldsymbol{x})=\sum\limits_i\chi_i(\boldsymbol{x})\hat{a}_i\\\hat{\psi}^\dagger(\boldsymbol{x})=\sum\limits_i\chi_i^\dagger(\boldsymbol{x})\hat{a}_i^\dagger\end{cases}$，根据定义，我们可知：

$$\begin{aligned}\{\hat{\psi}(\boldsymbol{x}),\hat{\psi}(\boldsymbol{x}')\}&=\{\sum_i\chi_i(\boldsymbol{x})\hat{a}_i,\sum_i\chi_i(\boldsymbol{x}')\hat{a}_i\}=\sum_i\chi_i(\boldsymbol{x})\hat{a}_i\sum_j\chi_j(\boldsymbol{x}')\hat{a}_j+\sum_i\chi_i(\boldsymbol{x}')\hat{a}_i\sum_j\chi_j(\boldsymbol{x})\hat{a}_j\\&=\sum_i\sum_j\chi_i(\boldsymbol{x})\chi_j(\boldsymbol{x}')\hat{a}_i\hat{a}_j+\sum_i\sum_j\chi_i(\boldsymbol{x}')\chi_j(\boldsymbol{x})\hat{a}_i\hat{a}_j=\sum_i\sum_j[\chi_i(\boldsymbol{x})\chi_j(\boldsymbol{x}')+\chi_i(\boldsymbol{x}')\chi_j(\boldsymbol{x})]\hat{a}_i\hat{a}_j\end{aligned}$$

$$\begin{aligned}\{\hat{\psi}^\dagger(\boldsymbol{x}),\hat{\psi}^\dagger(\boldsymbol{x}')\}&=\{\sum_i\chi_i^\dagger(\boldsymbol{x})\hat{a}_i^\dagger,\sum_i\chi_i^\dagger(\boldsymbol{x}')\hat{a}_i^\dagger\}=\sum_i\chi_i^\dagger(\boldsymbol{x})\hat{a}_i^\dagger\sum_j\chi_j^\dagger(\boldsymbol{x}')\hat{a}_j^\dagger+\sum_i\chi_i^\dagger(\boldsymbol{x}')\hat{a}_i^\dagger\sum_j\chi_j^\dagger(\boldsymbol{x})\hat{a}_j^\dagger\\&=\sum_i\sum_j\chi_i^\dagger(\boldsymbol{x})\chi_j^\dagger(\boldsymbol{x}')\hat{a}_i^\dagger\hat{a}_j^\dagger+\sum_i\sum_j\chi_i^\dagger(\boldsymbol{x}')\chi_j^\dagger(\boldsymbol{x})\hat{a}_i^\dagger\hat{a}_j^\dagger=\sum_i\sum_j[\chi_i^\dagger(\boldsymbol{x})\chi_j^\dagger(\boldsymbol{x}')+\chi_i^\dagger(\boldsymbol{x}')\chi_j^\dagger(\boldsymbol{x})]\hat{a}_i^\dagger\hat{a}_j^\dagger\end{aligned}$$

$$\begin{aligned}\{\hat{\psi}(\boldsymbol{x}),\hat{\psi}^\dagger(\boldsymbol{x}')\}&=\{\sum_i\chi_i(\boldsymbol{x})\hat{a}_i,\sum_i\chi_i^\dagger(\boldsymbol{x}')\hat{a}_i^\dagger\}=\sum_i\chi_i(\boldsymbol{x})\hat{a}_i\sum_j\chi_j^\dagger(\boldsymbol{x}')\hat{a}_j^\dagger+\sum_i\chi_i^\dagger(\boldsymbol{x}')\hat{a}_i^\dagger\sum_j\chi_j(\boldsymbol{x})\hat{a}_j\\&=\sum_i\sum_j\chi_i(\boldsymbol{x})\chi_j^\dagger(\boldsymbol{x}')\hat{a}_i\hat{a}_j^\dagger+\sum_i\sum_j\chi_i^\dagger(\boldsymbol{x}')\chi_j(\boldsymbol{x})\hat{a}_i^\dagger\hat{a}_j=\sum_i\sum_j[\chi_i(\boldsymbol{x})\chi_j^\dagger(\boldsymbol{x}')\hat{a}_i\hat{a}_j^\dagger+\chi_i^\dagger(\boldsymbol{x}')\chi_j(\boldsymbol{x})\hat{a}_i^\dagger\hat{a}_j]\\&=\sum_i\sum_j\chi_i(\boldsymbol{x})\chi_j^\dagger(\boldsymbol{x}')\hat{a}_i\hat{a}_j^\dagger+\sum_j\sum_i\chi_j^\dagger(\boldsymbol{x}')\chi_i(\boldsymbol{x})\hat{a}_j^\dagger\hat{a}_i=\sum_i\sum_j\chi_i(\boldsymbol{x})\chi_j^\dagger(\boldsymbol{x}')(\hat{a}_i\hat{a}_j^\dagger+\hat{a}_j^\dagger\hat{a}_i)\end{aligned}$$

从而对任意Slater行列式波函数$|\chi_k\dots\chi_l\rangle$，有

$$\begin{aligned}\{\hat{\psi}(\boldsymbol{x}),\hat{\psi}(\boldsymbol{x}^{'})\}|\chi_k\dots\chi_l\rangle &= \sum_i\sum_j[\chi_i(\boldsymbol{x})\chi_j(\boldsymbol{x}^{'})+\chi_i(\boldsymbol{x}^{'})\chi_j(\boldsymbol{x})]\cdot[\hat{a}_i\hat{a}_j|\chi_k\dots\chi_l\rangle] \\ &= \sum_i\sum_j[\chi_i(\boldsymbol{x})\chi_j(\boldsymbol{x}^{'})+\chi_i(\boldsymbol{x}^{'})\chi_j(\boldsymbol{x})]\cdot 0=0\end{aligned}$$

$$\begin{aligned}\{\hat{\psi}^{\dagger}(\boldsymbol{x}),\hat{\psi}^{\dagger}(\boldsymbol{x}^{'})\}|\chi_k\dots\chi_l\rangle &= \sum_i\sum_j[\chi_i^{\dagger}(\boldsymbol{x})\chi_j^{\dagger}(\boldsymbol{x}^{'})+\chi_i^{\dagger}(\boldsymbol{x}^{'})\chi_j^{\dagger}(\boldsymbol{x})]\cdot[\hat{a}_i^{\dagger}\hat{a}_j^{\dagger}|\chi_k\dots\chi_l\rangle] \\ &= \sum_i\sum_j[\chi_i^{\dagger}(\boldsymbol{x})\chi_j^{\dagger}(\boldsymbol{x}^{'})+\chi_i^{\dagger}(\boldsymbol{x}^{'})\chi_j^{\dagger}(\boldsymbol{x})]\cdot 0=0\end{aligned}$$

$$\begin{aligned}\{\hat{\psi}(\boldsymbol{x}),\hat{\psi}^{\dagger}(\boldsymbol{x}^{'})\}|\chi_k\dots\chi_l\rangle &= \sum_i\sum_j[\chi_i(\boldsymbol{x})\chi_j^{\dagger}(\boldsymbol{x}^{'})\hat{a}_i\hat{a}_j^{\dagger}+\chi_i^{\dagger}(\boldsymbol{x}^{'})\chi_j(\boldsymbol{x})\hat{a}_i^{\dagger}\hat{a}_j]|\chi_k\dots\chi_l\rangle \\ &= \sum_i\sum_j\chi_i(\boldsymbol{x})\chi_j^{\dagger}(\boldsymbol{x}^{'})(\hat{a}_i\hat{a}_j^{\dagger}+\hat{a}_j^{\dagger}\hat{a}_i)|\chi_k\dots\chi_l\rangle=\sum_i\sum_j\chi_i(\boldsymbol{x})\chi_j^{\dagger}(\boldsymbol{x}^{'})\{\hat{a}_i,\hat{a}_j^{\dagger}\}|\chi_k\dots\chi_l\rangle \\ &= \sum_i\sum_j\chi_i(\boldsymbol{x})\chi_j^{\dagger}(\boldsymbol{x}^{'})\delta_{ij}|\chi_k\dots\chi_l\rangle=\sum_i\chi_i(\boldsymbol{x})\chi_i^{\dagger}(\boldsymbol{x}^{'})|\chi_k\dots\chi_l\rangle=\delta(\boldsymbol{x}-\boldsymbol{x}^{'})|\chi_k\dots\chi_l\rangle\end{aligned}$$

因此有$\{\hat{\psi}(\boldsymbol{x}),\hat{\psi}(\boldsymbol{x}^{'})\}=0$，$\{\hat{\psi}^{\dagger}(\boldsymbol{x}),\hat{\psi}^{\dagger}(\boldsymbol{x}^{'})\}=0$，$\{\hat{\psi}(\boldsymbol{x}),\hat{\psi}^{\dagger}(\boldsymbol{x}^{'})\}=\delta(\boldsymbol{x}-\boldsymbol{x}^{'})$