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）

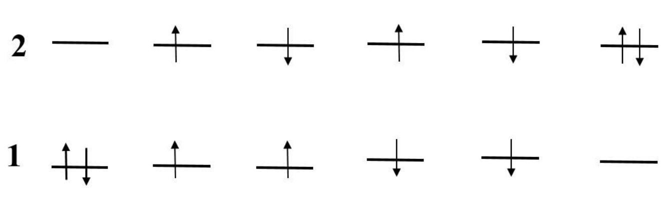
证明：首先证明行列式波函数是$\hat{S}_z$的本征态，由于$\hat{S}_z=\sum_u \hat{s}_{z,u}$，因此设$\chi_1,\chi_2,\ldots,\chi_{N-N_s-1},\chi_{N-N_s}$为非单占轨道（$N-N_s$为偶数），且$\chi_{2i-1}=\psi_{2i-1}\alpha$，$\chi_{2i}=\psi_{2i}\beta$；而$\chi_{N-N_s+1},\chi_{N-N_s+2},\ldots,\chi_{N-1},\chi_N$为单占轨道（特别的，若$N_s=0$，则无单占轨道），则

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

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$\hat{S}_+=\sum_u \hat{s}_{u,+}$，$\hat{S}_-=\sum_u \hat{s}_{u,-}$，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

$$
\begin{aligned}
\hat{S}_+\hat{S}_-|\chi_1\chi_2\ldots\chi_N\rangle &= \hat{S}_+(\hat{S}_-|\chi_1\chi_2\ldots\chi_N\rangle)=\hat{S}_+\sum_{u=1}^{N}\hat{s}_{u,-}\cdot\frac{1}{\sqrt{N!}}\sum_P(-1)^P\chi_{P_1}(\boldsymbol{x}_1)\chi_{P_2}(\boldsymbol{x}_2)\ldots\chi_{P_N}(\boldsymbol{x}_N)\\
&=
\end{aligned}
$$

练习2：写出下图电子构型的哈密尔顿算符的期望值



$|1\bar{1}\rangle$ (1) $|12\rangle$ (2) $|1\bar{2}\rangle$ (3) $|\bar{1}2\rangle$ (4) $|\bar{1}\bar{2}\rangle$ (5) $|2\bar{2}\rangle$ (6)

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

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

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

$$\begin{aligned}\hat{S}_+\hat{S}_-\Theta_1(1,2)&=(\hat{s}_{1,+}+\hat{s}_{2,+})(\hat{s}_{1,-}+\hat{s}_{2,-})\Theta_1(1,2)=(\hat{s}_{1,+}+\hat{s}_{2,+})[(\hat{s}_{1,-}+\hat{s}_{2,-})\Theta_1(1,2)]\\&=(\hat{s}_{1,+}+\hat{s}_{2,+})\cdot2^{-\frac{1}{2}}\{[\hat{s}_{1,-}\alpha(1)]\beta(2)-\alpha(2)[\hat{s}_{1,-}\beta(1)]+\alpha(1)[\hat{s}_{2,-}\beta(2)]-[\hat{s}_{2,-}\alpha(2)]\beta(1)\}\\&=(\hat{s}_{1,+}+\hat{s}_{2,+})\cdot2^{-\frac{1}{2}}\{\hbar\beta(1)\cdot\beta(2)-\alpha(2)\cdot0+\alpha(1)\cdot0-\hbar\beta(2)\cdot\beta(1)\}=0\end{aligned}$$

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

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

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

$$\begin{aligned}\hat{S}_+\hat{S}_-\Theta_2(1,2)&=(\hat{s}_{1,+}+\hat{s}_{2,+})(\hat{s}_{1,-}+\hat{s}_{2,-})\Theta_2(1,2)=(\hat{s}_{1,+}+\hat{s}_{2,+})[(\hat{s}_{1,-}+\hat{s}_{2,-})\Theta_2(1,2)]\\&=(\hat{s}_{1,+}+\hat{s}_{2,+})\cdot2^{-\frac{1}{2}}\{[\hat{s}_{1,-}\alpha(1)]\beta(2)+\alpha(2)[\hat{s}_{1,-}\beta(1)]+\alpha(1)[\hat{s}_{2,-}\beta(2)]+[\hat{s}_{2,-}\alpha(2)]\beta(1)\}\\&=(\hat{s}_{1,+}+\hat{s}_{2,+})\cdot2^{-\frac{1}{2}}\{\hbar\beta(1)\cdot\beta(2)+\alpha(2)\cdot0+\alpha(1)\cdot0+\hbar\beta(2)\cdot\beta(1)\}=(\hat{s}_{1,+}+\hat{s}_{2,+})[\sqrt{2}\hbar\beta(1)\beta(2)]\\&=\sqrt{2}\hbar\{[\hat{s}_{1,+}\beta(1)]\beta(2)+\beta(1)[\hat{s}_{2,+}\beta(2)]\}=\sqrt{2}\hbar\{\hbar\alpha(1)\cdot\beta(2)+\beta(1)\cdot\hbar\alpha(2)\}\\&=\sqrt{2}\hbar^2\{\alpha(1)\beta(2)+\beta(1)\alpha(2)\}=2\hbar^2\Theta_2(1,2)=1\cdot(1+1)\hbar\Theta_2(1,2)\end{aligned}$$

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$\langle\hat{S}^2\rangle_{\mathrm{UHF}}=\langle\hat{S}^2\rangle_{\mathrm{exact}}+N_\beta-\sum_{i=1}^{N_\alpha}\sum_{j=1}^{N_\beta}|S_{ij}^{\alpha\beta}|^2$

证明:

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:

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:

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: