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$\hat{S}_-\hat{S}_+=\sum\limits_u\hat{s}_{u,-}\cdot\sum\limits_v\hat{s}_{v,+}=\sum\limits_u\hat{s}_{u,-}\hat{s}_{u,+}+\sum\limits_{u\neq v}\hat{s}_{u,-}\hat{s}_{v,+}$，记$\hat{O}_1=\sum\limits_u\hat{s}_{u,-}\hat{s}_{u,+}$，$\hat{O}_2=\sum\limits_{u\neq v}\hat{s}_{u,-}\hat{s}_{v,+}$，$\chi_{2i-1}^{\beta}=\psi_i\beta$，$\chi_{2i}^{\alpha}=\psi_i\alpha$，现在分情况讨论：

（1）若为闭壳层行列式波函数，则：

$$\begin{aligned}
\hat{O}_1|\chi_1\chi_2\ldots\chi_N\rangle &= \sum_{u=1}^{N}\hat{s}_{u,-}\hat{s}_{u,+}|\chi_1\chi_2\ldots\chi_N\rangle=\sum_{u=1}^{N}\hat{s}_{u,-}(\hat{s}_{u,+}|\chi_1\chi_2\ldots\chi_N\rangle)=\sum_{u=1}^{\frac{N}{2}}\hbar\hat{s}_{2u,-}|\chi_1\chi_2\ldots\chi_{2u}^{\alpha}\ldots\chi_N\rangle\\
&=\sum_{u=1}^{\frac{N}{2}}\hbar^2|\chi_1\chi_2\ldots\chi_N\rangle=\frac{N\hbar^2}{2}|\chi_1\chi_2\ldots\chi_N\rangle
\end{aligned}$$

$$
\begin{aligned}
&\hat{O}_2|\chi_1\chi_2\dots\chi_N\rangle = \sum_{u\neq v}\hat{s}_{u,-}\hat{s}_{v,+}|\chi_1\chi_2\dots\chi_N\rangle \\
&= \sum_{u=1}^{\frac{N}{2}}\sum_{\substack{v=1\\u\neq v}}^{\frac{N}{2}}\hat{s}_{2u-1,-}\cdot(\hat{s}_{2v-1,+}|\chi_1\chi_2\dots\chi_N\rangle) + \sum_{u=1}^{\frac{N}{2}}\sum_{v=1}^{\frac{N}{2}}\hat{s}_{2u-1,-}\cdot(\hat{s}_{2v,+}|\chi_1\chi_2\dots\chi_N\rangle) \\
&\quad + \sum_{u=1}^{\frac{N}{2}}\sum_{v=1}^{\frac{N}{2}}\hat{s}_{2u,-}\cdot(\hat{s}_{2v-1,+}|\chi_1\chi_2\dots\chi_N\rangle) + \sum_{u=1}^{\frac{N}{2}}\sum_{\substack{v=1\\u\neq v}}^{\frac{N}{2}}\hat{s}_{2u,-}\cdot(\hat{s}_{2v,+}|\chi_1\chi_2\dots\chi_N\rangle) \\
&= \sum_{u=1}^{\frac{N}{2}}\sum_{\substack{v=1\\u\neq v}}^{\frac{N}{2}}\hat{s}_{2u-1,-}\cdot 0 + \sum_{u=1}^{\frac{N}{2}}\sum_{v=1}^{\frac{N}{2}}\hbar\hat{s}_{2u-1,-}|\chi_1\chi_2\dots\chi_{2v}^{\alpha}\dots\chi_N\rangle + \sum_{u=1}^{\frac{N}{2}}\sum_{v=1}^{\frac{N}{2}}\hat{s}_{2u,-}\cdot 0 + \sum_{u=1}^{\frac{N}{2}}\sum_{\substack{v=1\\u\neq v}}^{\frac{N}{2}}\hbar\hat{s}_{2u,-}|\chi_1\chi_2\dots\chi_{2v}^{\alpha}\dots\chi_N\rangle \\
&= \sum_{u=1}^{\frac{N}{2}}\sum_{v=1}^{\frac{N}{2}}\hbar^2|\chi_1\chi_2\dots\chi_{2u-1}^{\beta}\dots\chi_{2v}^{\alpha}\dots\chi_N\rangle + \sum_{u=1}^{\frac{N}{2}}\sum_{\substack{v=1\\u\neq v}}^{\frac{N}{2}}\hbar\cdot 0 = \hbar^2\sum_{u=1}^{\frac{N}{2}}\sum_{v=1}^{\frac{N}{2}}|\chi_1\chi_2\dots\chi_{2u-1}^{\beta}\dots\chi_{2v}^{\alpha}\dots\chi_N\rangle
\end{aligned}
$$

为求出$\hat{O}_2$的本征值，我们左乘Slater行列式$\langle\chi_1\chi_2\dots\chi_N|$，得:

$$
\begin{aligned}
&\langle\chi_1\chi_2\dots\chi_N|\hat{O}_2|\chi_1\chi_2\dots\chi_N\rangle = \langle\chi_1\chi_2\dots\chi_N|\cdot\hbar^2\sum_{u=1}^{\frac{N}{2}}\sum_{v=1}^{\frac{N}{2}}|\chi_1\chi_2\dots\chi_{2u-1}^{\beta}\dots\chi_{2v}^{\alpha}\dots\chi_N\rangle \\
&= \frac{\hbar^2}{2!}\sum_{u=1}^{\frac{N}{2}}\sum_{v=1}^{\frac{N}{2}}\iint\begin{vmatrix}\chi_{2u-1}^*(\boldsymbol{x}_1) & \chi_{2v}^*(\boldsymbol{x}_1)\\ \chi_{2u-1}^*(\boldsymbol{x}_2) & \chi_{2v}^*(\boldsymbol{x}_2)\end{vmatrix}\begin{vmatrix}\chi_{2u-1}^{\beta}(\boldsymbol{x}_1) & \chi_{2v}^{\alpha}(\boldsymbol{x}_1)\\ \chi_{2u-1}^{\beta}(\boldsymbol{x}_2) & \chi_{2v}^{\alpha}(\boldsymbol{x}_2)\end{vmatrix}d\boldsymbol{x}_1d\boldsymbol{x}_2 \\
&= \frac{\hbar^2}{2}\sum_{u=1}^{\frac{N}{2}}\sum_{v=1}^{\frac{N}{2}}\iiiint\begin{vmatrix}\psi_u^*(\boldsymbol{r}_1)\alpha^*(s_1) & \psi_v^*(\boldsymbol{r}_1)\beta^*(s_1)\\ \psi_u^*(\boldsymbol{r}_2)\alpha^*(s_2) & \psi_v^*(\boldsymbol{r}_2)\beta^*(s_2)\end{vmatrix}\begin{vmatrix}\psi_u(\boldsymbol{r}_1)\beta(s_1) & \psi_v(\boldsymbol{r}_1)\alpha(s_1)\\ \psi_u(\boldsymbol{r}_2)\beta(s_2) & \psi_v(\boldsymbol{r}_2)\alpha(s_2)\end{vmatrix}d\boldsymbol{r}_1d\boldsymbol{r}_2ds_1ds_2 \\
&= -\frac{\hbar^2}{2}\sum_{u=1}^{\frac{N}{2}}2\iint|\psi_u(\boldsymbol{r}_1)|^2|\psi_u(\boldsymbol{r}_2)|^2d\boldsymbol{r}_1d\boldsymbol{r}_2 = -\frac{\hbar^2}{2}\cdot 2\cdot\frac{N}{2} = -\frac{N\hbar^2}{2}
\end{aligned}
$$

从而有$\hat{O}_2 = -\frac{N\hbar^2}{2}\hat{I}$，因此

$$
\hat{S}_-\hat{S}_+|\chi_1\chi_2\dots\chi_N\rangle = \hat{O}_1|\chi_1\chi_2\dots\chi_N\rangle + \hat{O}_2|\chi_1\chi_2\dots\chi_N\rangle = \frac{N\hbar^2}{2}|\chi_1\chi_2\dots\chi_N\rangle + (-\frac{N\hbar^2}{2}|\chi_1\chi_2\dots\chi_N\rangle) = 0
$$

$$
\hat{S}^2|\chi_1\chi_2\dots\chi_N\rangle = (\hat{S}_-\hat{S}_+ + \hbar\hat{S}_z + \hat{S}_z^2)|\chi_1\chi_2\dots\chi_N\rangle = 0
$$

即自旋量子数$S=0$

（2）若单占据轨道全部取自旋向上，则:

$$
\begin{aligned}
\hat{O}_1|\chi_1\chi_2\dots\chi_N\rangle &= \sum_{u=1}^{N}\hat{s}_{u,-}\hat{s}_{u,+}|\chi_1\chi_2\dots\chi_N\rangle = \sum_{u=1}^{N-N_s}\hat{s}_{u,-}(\hat{s}_{u,+}|\chi_1\chi_2\dots\chi_N\rangle) + \sum_{u=N-N_s+1}^{N}\hat{s}_{u,-}(\hat{s}_{u,+}|\chi_1\chi_2\dots\chi_N\rangle) \\
&= \sum_{u=1}^{\frac{N-N_s}{2}}\hbar\hat{s}_{2u,-}|\chi_1\chi_2\dots\chi_{2u}^{\alpha}\dots\chi_N\rangle = \sum_{u=1}^{\frac{N-N_s}{2}}\hbar^2|\chi_1\chi_2\dots\chi_N\rangle = \frac{(N-N_s)\hbar^2}{2}
\end{aligned}
$$

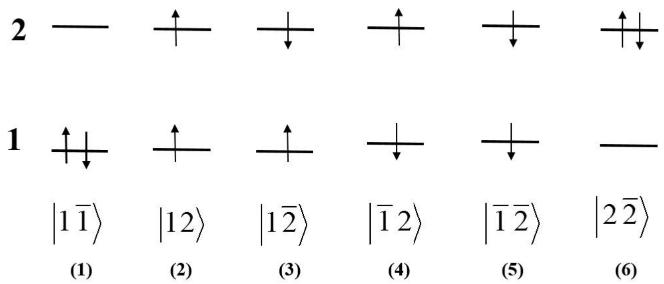
$$
\hat{O}_2|\chi_1\chi_2\dots\chi_N\rangle
$$

（3）若单占据轨道全部取自旋向下，则:

$$\begin{aligned}\hat{O}_1|\chi_1\chi_2\dots\chi_N\rangle &= \sum_{u=1}^{N}\hat{s}_{u,-}\hat{s}_{u,+}|\chi_1\chi_2\dots\chi_N\rangle = \sum_{u=1}^{N-N_s}\hat{s}_{u,-}(\hat{s}_{u,+}|\chi_1\chi_2\dots\chi_N\rangle) + \sum_{u=N-N_s+1}^{N}\hat{s}_{u,-}(\hat{s}_{u,+}|\chi_1\chi_2\dots\chi_N\rangle)\\ &= \sum_{u=1}^{\frac{N-N_s}{2}}\hbar\hat{s}_{2u,-}|\chi_1\chi_2\dots\chi_{2u}^{\alpha}\dots\chi_N\rangle + \sum_{u=N-N_s+1}^{N}\hbar\hat{s}_{u,-}|\chi_1\chi_2\dots\chi_u^{\alpha}\dots\chi_N\rangle\\ &= \sum_{u=1}^{\frac{N-N_s}{2}}\hbar^2|\chi_1\chi_2\dots\chi_N\rangle + \sum_{u=N-N_s+1}^{N}\hbar^2|\chi_1\chi_2\dots\chi_N\rangle = [\frac{(N-N_s)}{2}+N_s]\hbar^2 = \frac{(N+N_s)\hbar^2}{2}\end{aligned}$$

$$\hat{O}_2|\chi_1\chi_2\dots\chi_N\rangle$$

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

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

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

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
$\hat{S}_-\hat{S}_+=\sum\limits_u\hat{s}_{u,-}\cdot\sum\limits_v\hat{s}_{v,+}=\sum\limits_u\hat{s}_{u,-}\hat{s}_{u,+}+\sum\limits_{u\neq v}\hat{s}_{u,-}\hat{s}_{v,+}$，记$\hat{O}_1=\sum\limits_u\hat{s}_{u,-}\hat{s}_{u,+}$，
$\hat{O}_2=\sum\limits_u\hat{s}_{u,-}\hat{s}_{u,+}+\sum\limits_{u\neq v}\hat{s}_{u,-}\hat{s}_{v,+}$，$N=N_\alpha+N_\beta$，结合UHF下轨道的定义
$\begin{cases}\chi_{2i-1}(\boldsymbol{x})=\psi_i^\alpha(\boldsymbol{r})\alpha(s)\\\chi_{2i}(\boldsymbol{x})=\psi_i^\beta(\boldsymbol{r})\beta(s)\end{cases}$，以及上升算符与下降算符的互为厄米共轭的关系，得（记
$\begin{cases}\chi_{2i-1}^\beta(\boldsymbol{x})=\psi_i^\alpha(\boldsymbol{r})\beta(s)\\\chi_{2i}^\alpha(\boldsymbol{x})=\psi_i^\beta(\boldsymbol{r})\alpha(s)\end{cases}$）：

$$\begin{aligned}
&\langle\chi_1\chi_2\dots\chi_N|\hat{O}_1|\chi_1\chi_2\dots\chi_N\rangle=\sum_u\langle\chi_1\chi_2\dots\chi_N|\hat{s}_{u,-}\hat{s}_{u,+}|\chi_1\chi_2\dots\chi_N\rangle\\
&=\sum_{u=1}^{N_\alpha}\langle\chi_1\chi_2\dots\chi_N|\hat{s}_{2u-1,-}\hat{s}_{2u-1,+}|\chi_1\chi_2\dots\chi_N\rangle+\sum_{u=1}^{N_\beta}\langle\chi_1\chi_2\dots\chi_N|\hat{s}_{2u,-}\hat{s}_{2u,+}|\chi_1\chi_2\dots\chi_N\rangle\\
&=\sum_{u=1}^{N_\alpha}\langle\chi_1\chi_2\dots\chi_N|\cdot[\hat{s}_{2u-1,-}(\hat{s}_{2u-1,+}|\chi_1\chi_2\dots\chi_N\rangle)]+\sum_{u=1}^{N_\beta}\langle\chi_1\chi_2\dots\chi_N|\cdot[\hat{s}_{2u,-}(\hat{s}_{2u,+}|\chi_1\chi_2\dots\chi_N\rangle)]\\
&=\sum_{u=1}^{N_\alpha}\langle\chi_1\chi_2\dots\chi_N|\cdot[\hat{s}_{2u-1,-}\cdot 0]+\sum_{u=1}^{N_\beta}\langle\chi_1\chi_2\dots\chi_N|\cdot[\hbar\hat{s}_{2u,-}|\chi_1\chi_2\dots\chi_{2u}^\alpha\dots\chi_N\rangle]\\
&=\sum_{u=1}^{N_\beta}\langle\chi_1\chi_2\dots\chi_N|\cdot\hbar^2|\chi_1\chi_2\dots\chi_N\rangle=N_\beta\hbar^2
\end{aligned}$$

$$
\begin{aligned}
&\langle\chi_1\chi_2\dots\chi_N|\hat{O}_2|\chi_1\chi_2\dots\chi_N\rangle=\sum_{u\neq v}\langle\chi_1\chi_2\dots\chi_N|\hat{s}_{u,-}\hat{s}_{v,+}|\chi_1\chi_2\dots\chi_N\rangle\\
&=\sum_{u=1}^{N_\alpha}\sum_{\substack{v=1\\u\neq v}}^{N_\alpha}\langle\chi_1\chi_2\dots\chi_N|\cdot[\hat{s}_{2u-1,-}(\hat{s}_{2v-1,+}|\chi_1\chi_2\dots\chi_N\rangle)]+\sum_{u=1}^{N_\alpha}\sum_{v=1}^{N_\beta}\langle\chi_1\chi_2\dots\chi_N|\cdot[\hat{s}_{2u-1,-}(\hat{s}_{2v,+}|\chi_1\chi_2\dots\chi_N\rangle)]\\
&\quad+\sum_{u=1}^{N_\beta}\sum_{v=1}^{N_\alpha}\langle\chi_1\chi_2\dots\chi_N|\cdot[\hat{s}_{2u,-}(\hat{s}_{2v-1,+}|\chi_1\chi_2\dots\chi_N\rangle)]+\sum_{u=1}^{N_\beta}\sum_{\substack{v=1\\u\neq v}}^{N_\beta}\langle\chi_1\chi_2\dots\chi_N|\cdot[\hat{s}_{2u,-}(\hat{s}_{2v,+}|\chi_1\chi_2\dots\chi_N\rangle)]\\
&=\sum_{u=1}^{N_\alpha}\sum_{\substack{v=1\\u\neq v}}^{N_\alpha}\langle\chi_1\chi_2\dots\chi_N|\cdot[\hat{s}_{2u-1,-}\cdot 0]+\sum_{u=1}^{N_\alpha}\sum_{v=1}^{N_\beta}\langle\chi_1\chi_2\dots\chi_N|\cdot[\hbar\hat{s}_{2u-1,-}|\chi_1\chi_2\dots\chi_{2v}^{\alpha}\dots\chi_N\rangle)]\\
&\quad+\sum_{u=1}^{N_\beta}\sum_{v=1}^{N_\alpha}\langle\chi_1\chi_2\dots\chi_N|\cdot[\hat{s}_{2u,-}\cdot 0]+\sum_{u=1}^{N_\beta}\sum_{\substack{v=1\\u\neq v}}^{N_\beta}\langle\chi_1\chi_2\dots\chi_N|\cdot[\hbar\hat{s}_{2u,-}|\chi_1\chi_2\dots\chi_{2v}^{\alpha}\dots\chi_N\rangle)]\\
&=\sum_{u=1}^{N_\alpha}\sum_{v=1}^{N_\beta}\langle\chi_1\chi_2\dots\chi_N|\cdot\hbar^2|\chi_1\chi_2\dots\chi_{2u-1}^{\beta}\dots\chi_{2v}^{\alpha}\dots\chi_N\rangle+\sum_{u=1}^{N_\beta}\sum_{\substack{v=1\\u\neq v}}^{N_\beta}\langle\chi_1\chi_2\dots\chi_N|\cdot 0\\
&=\frac{\hbar^2}{2!}\sum_{u=1}^{N_\alpha}\sum_{v=1}^{N_\beta}\iiiint\begin{vmatrix}\psi_u^{\alpha,*}(\boldsymbol{r}_1)\alpha^*(s_1) & \psi_v^{\beta,*}(\boldsymbol{r}_1)\beta^*(s_1)\\ \psi_u^{\alpha,*}(\boldsymbol{r}_2)\alpha^*(s_2) & \psi_v^{\beta,*}(\boldsymbol{r}_2)\beta^*(s_2)\end{vmatrix}\begin{vmatrix}\psi_u^{\alpha}(\boldsymbol{r}_1)\beta(s_1) & \psi_v^{\beta}(\boldsymbol{r}_1)\alpha(s_1)\\ \psi_u^{\alpha}(\boldsymbol{r}_2)\beta(s_2) & \psi_v^{\beta}(\boldsymbol{r}_2)\alpha(s_2)\end{vmatrix}d\boldsymbol{r}_1d\boldsymbol{r}_2ds_1ds_2\\
&=-\frac{\hbar^2}{2!}\sum_{u=1}^{N_\alpha}\sum_{v=1}^{N_\beta}(S_{vu}^{\beta\alpha}S_{uv}^{\alpha\beta}+S_{uv}^{\alpha\beta}S_{vu}^{\beta\alpha})=-\hbar^2\sum_{u=1}^{N_\alpha}\sum_{v=1}^{N_\beta}|S_{uv}^{\alpha\beta}|^2
\end{aligned}
$$

从而有

$$
\langle\chi_1\chi_2\dots\chi_N|\hat{S}_-\hat{S}_+|\chi_1\chi_2\dots\chi_N\rangle=\langle\chi_1\chi_2\dots\chi_N|\hat{O}_1|\chi_1\chi_2\dots\chi_N\rangle+\langle\chi_1\chi_2\dots\chi_N|\hat{O}_2|\chi_1\chi_2\dots\chi_N\rangle=\hbar^2(N_\beta-\sum_{u=1}^{N_\alpha}\sum_{v=1}^{N_\beta}|S_{uv}^{\alpha\beta}|^2)
$$

$$
\begin{aligned}
\langle\hat{S}^2\rangle_{\text{UHF}}&=\langle\chi_1\chi_2\dots\chi_N|\hat{S}_-\hat{S}_+|\chi_1\chi_2\dots\chi_N\rangle+\frac{N_\alpha-N_\beta}{2}(\frac{N_\alpha-N_\beta}{2}+1)\hbar^2\\
&=\hbar^2[\frac{N_\alpha-N_\beta}{2}(\frac{N_\alpha-N_\beta}{2}+1)+N_\beta-\sum_{u=1}^{N_\alpha}\sum_{v=1}^{N_\beta}|S_{uv}^{\alpha\beta}|^2]
\end{aligned}
$$

记$\langle\hat{S}^2\rangle_{\text{exact}}=\frac{N_\alpha-N_\beta}{2}(\frac{N_\alpha-N_\beta}{2}+1)\hbar^2$，当采用原子单位制时，$\hbar=1$，即得到自旋污染的表达式

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

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

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

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

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

因此

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

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

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

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

因此

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

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