课堂练习

练习1：如果用6-31g(d,p)基组来描述水分子，请问需要多少个CGF（收缩型高斯基函数）？需要多少个GTO（高斯基函数）？

解：6-31g(d,p)基组意为：内层电子用一个收缩度为6的CGF描述，价层电子用两个CGF描述，其中一个收缩度为3，另一个收缩度为1（即不收缩）；此外，对H、He原子加上一层不收缩的（笛卡尔型）p极化轨道（p_x，p_y，p_z），对重原子（自Li开始的原子）加上一层不收缩的（笛卡尔型）d极化轨道（d_{xx}，d_{yy}，d_{zz}，d_{xy}，d_{xz}，d_{yz}）。对于水分子而言，两个氢原子均只有价层电子1s，每个氢原子所需的CGF为2（1s轨道）+3（p极化轨道）=5；氧原子内层电子为1s，价层电子为2s和2p，因此所需的CGF为1（1s轨道）+2×（1+3）（2s和2p轨道）+6（d极化轨道）=15；从而水分子总计CGF数为2×5+15=25。如果是计算水分子的GTO数，则每个氢原子的GTO为（3+1）（1s轨道）+3=7，氧原子的GTO为6（1s轨道）+（3+1）×（1+3）（2s和2p轨道）+6（d极化轨道）=28，从而总GTO数为7×2+28=42。

练习2：推导如下结论：Slater行列式波函数$|\chi_1 \dots \chi_N\rangle$的一阶和二阶约化密度矩阵具有如下形式

$$\gamma_1(\boldsymbol{x}_1;\boldsymbol{x}_1^{'}) = \sum_{a=1}^{N}\chi_a(\boldsymbol{x}_1)\chi_a^*(\boldsymbol{x}_1^{'})$$
$$\gamma_2(\boldsymbol{x}_1,\boldsymbol{x}_2;\boldsymbol{x}_1^{'},\boldsymbol{x}_2^{'}) = \frac{1}{2}[\gamma_1(\boldsymbol{x}_1;\boldsymbol{x}_1^{'})\gamma_1(\boldsymbol{x}_2;\boldsymbol{x}_2^{'}) - \gamma_1(\boldsymbol{x}_1;\boldsymbol{x}_2^{'})\gamma_1(\boldsymbol{x}_2;\boldsymbol{x}_1^{'})]$$

解：根据密度矩阵和一阶约化密度的定义

$$\begin{aligned}\gamma_N(\boldsymbol{x}_1^{'},\boldsymbol{x}_2^{'},\dots,\boldsymbol{x}_N^{'};\boldsymbol{x}_1,\boldsymbol{x}_2,\dots,\boldsymbol{x}_N) &= \Phi_N(\boldsymbol{x}_1^{'},\boldsymbol{x}_2^{'},\dots,\boldsymbol{x}_N^{'})\Phi_N^*(\boldsymbol{x}_1,\boldsymbol{x}_2,\dots,\boldsymbol{x}_N)\\ \gamma_1(\boldsymbol{x}_1^{'};\boldsymbol{x}_1) &= N\int\cdots\int\gamma_N(\boldsymbol{x}_1^{'},\boldsymbol{x}_2,\dots,\boldsymbol{x}_N;\boldsymbol{x}_1,\boldsymbol{x}_2,\dots,\boldsymbol{x}_N)d\boldsymbol{x}_2\dots d\boldsymbol{x}_N\\ &= N\int\cdots\int\Phi_N(\boldsymbol{x}_1^{'},\boldsymbol{x}_2,\dots,\boldsymbol{x}_N)\Phi_N^*(\boldsymbol{x}_1,\boldsymbol{x}_2,\dots,\boldsymbol{x}_N)d\boldsymbol{x}_2\dots d\boldsymbol{x}_N\end{aligned}$$

结合Slater行列式波函数的含义

$$\Phi_N(\boldsymbol{x}_1,\boldsymbol{x}_2,\dots,\boldsymbol{x}_N) = |\chi_1\dots\chi_N\rangle = \frac{1}{\sqrt{N!}}\begin{vmatrix}\chi_1(\boldsymbol{x}_1) & \chi_2(\boldsymbol{x}_1) & \dots & \chi_N(\boldsymbol{x}_1)\\ \chi_1(\boldsymbol{x}_2) & \chi_2(\boldsymbol{x}_2) & \dots & \chi_N(\boldsymbol{x}_2)\\ \vdots & \vdots & \ddots & \vdots\\ \chi_1(\boldsymbol{x}_N) & \chi_2(\boldsymbol{x}_N) & \dots & \chi_N(\boldsymbol{x}_N)\end{vmatrix} = \frac{1}{\sqrt{N!}}\sum_{i=1}^{N}(-1)^{1+i}\chi_i(\boldsymbol{x}_1)\mathrm{coef}[\chi_i(\boldsymbol{x}_1)]$$

其中$\mathrm{coef}[\chi_i(\boldsymbol{x}_1)]$为提出$\chi_i(\boldsymbol{x}_1)$的代数余子式，我们有：

$$\begin{aligned}\gamma_1(\boldsymbol{x}_1;\boldsymbol{x}_1^{'}) &= N\int\cdots\int\Phi_N(\boldsymbol{x}_1,\boldsymbol{x}_2,\dots,\boldsymbol{x}_N)\Phi_N^*(\boldsymbol{x}_1^{'},\boldsymbol{x}_2,\dots,\boldsymbol{x}_N)d\boldsymbol{x}_2\dots d\boldsymbol{x}_N\\ &= N\int\cdots\int\frac{1}{\sqrt{N!}}\sum_{i=1}^{N}(-1)^{1+i}\chi_i(\boldsymbol{x}_1)\mathrm{coef}[\chi_i(\boldsymbol{x}_1)]\cdot\frac{1}{\sqrt{N!}}\sum_{i^{'}=1}^{N}(-1)^{1+i^{'}}\chi_{i^{'}}^*(\boldsymbol{x}_1^{'})\mathrm{coef}[\chi_{i^{'}}^*(\boldsymbol{x}_1^{'})]d\boldsymbol{x}_2\dots d\boldsymbol{x}_N\\ &= \frac{1}{(N-1)!}\int\cdots\int\sum_{i=1}^{N}\sum_{i^{'}=1}^{N}(-1)^{2+i+i^{'}}\chi_i(\boldsymbol{x}_1)\chi_{i^{'}}^*(\boldsymbol{x}_1^{'})\mathrm{coef}[\chi_i(\boldsymbol{x}_1)]\mathrm{coef}[\chi_{i^{'}}^*(\boldsymbol{x}_1^{'})]d\boldsymbol{x}_2\dots d\boldsymbol{x}_N\\ &= \frac{1}{(N-1)!}\int\cdots\int\sum_{i=1}^{N}\chi_i(\boldsymbol{x}_1)\chi_i^*(\boldsymbol{x}_1^{'})\mathrm{coef}[\chi_i(\boldsymbol{x}_1)]\mathrm{coef}[\chi_i^*(\boldsymbol{x}_1^{'})]d\boldsymbol{x}_2\dots d\boldsymbol{x}_N\ \text{（利用波函数正交性）}\\ &= \frac{1}{(N-1)!}\sum_{i=1}^{N}\chi_i(\boldsymbol{x}_1)\chi_i^*(\boldsymbol{x}_1^{'})\cdot(N-1)! = \sum_{i=1}^{N}\chi_i(\boldsymbol{x}_1)\chi_i^*(\boldsymbol{x}_1^{'})\end{aligned}$$

同理，对于二阶约化密度，我们有：

$$
\begin{aligned}
\gamma_1(\boldsymbol{x}_1,\boldsymbol{x}_2;\boldsymbol{x}_1^{'},\boldsymbol{x}_2^{'}) &= \frac{N(N-1)}{2}\int\cdots\int \gamma_N(\boldsymbol{x}_1,\boldsymbol{x}_2,\ldots,\boldsymbol{x}_N;\boldsymbol{x}_1^{'},\boldsymbol{x}_2^{'},\ldots,\boldsymbol{x}_N)d\boldsymbol{x}_3\ldots d\boldsymbol{x}_N \\
&= \frac{N(N-1)}{2}\int\cdots\int \Phi_N(\boldsymbol{x}_1,\boldsymbol{x}_2,\ldots,\boldsymbol{x}_N)\Phi_N^*(\boldsymbol{x}_1^{'},\boldsymbol{x}_2^{'},\ldots,\boldsymbol{x}_N)d\boldsymbol{x}_3\ldots d\boldsymbol{x}_N \\
&= \frac{N(N-1)}{2}\int\cdots\int \frac{1}{\sqrt{N!}}\sum_{1\le i<j\le N}(-1)^{1+i+2+j}\begin{vmatrix}\chi_i(\boldsymbol{x}_1) & \chi_j(\boldsymbol{x}_1)\\ \chi_i(\boldsymbol{x}_2) & \chi_j(\boldsymbol{x}_2)\end{vmatrix}\mathrm{coef}\begin{bmatrix}\chi_i(\boldsymbol{x}_1) & \chi_j(\boldsymbol{x}_1)\\ \chi_i(\boldsymbol{x}_2) & \chi_j(\boldsymbol{x}_2)\end{bmatrix} \\
&\quad\cdot\frac{1}{\sqrt{N!}}\sum_{1\le i^{'}<j^{'}\le N}(-1)^{1+i^{'}+2+j^{'}}\begin{vmatrix}\chi_i^*(\boldsymbol{x}_1^{'}) & \chi_j^*(\boldsymbol{x}_1^{'})\\ \chi_i^*(\boldsymbol{x}_2^{'}) & \chi_j^*(\boldsymbol{x}_2^{'})\end{vmatrix}\mathrm{coef}\begin{bmatrix}\chi_i^*(\boldsymbol{x}_1^{'}) & \chi_j^*(\boldsymbol{x}_1^{'})\\ \chi_i^*(\boldsymbol{x}_2^{'}) & \chi_j^*(\boldsymbol{x}_2^{'})\end{bmatrix}d\boldsymbol{x}_3\ldots d\boldsymbol{x}_N \\
&= \frac{1}{2(N-2)!}\int\cdots\int\sum_{1\le i<j\le N}\begin{vmatrix}\chi_i(\boldsymbol{x}_1) & \chi_j(\boldsymbol{x}_1)\\ \chi_i(\boldsymbol{x}_2) & \chi_j(\boldsymbol{x}_2)\end{vmatrix}\begin{vmatrix}\chi_i^*(\boldsymbol{x}_1^{'}) & \chi_j^*(\boldsymbol{x}_1^{'})\\ \chi_i^*(\boldsymbol{x}_2^{'}) & \chi_j^*(\boldsymbol{x}_2^{'})\end{vmatrix} \\
&\quad\cdot\mathrm{coef}\begin{bmatrix}\chi_i(\boldsymbol{x}_1) & \chi_j(\boldsymbol{x}_1)\\ \chi_i(\boldsymbol{x}_2) & \chi_j(\boldsymbol{x}_2)\end{bmatrix}\mathrm{coef}\begin{bmatrix}\chi_i^*(\boldsymbol{x}_1^{'}) & \chi_j^*(\boldsymbol{x}_1^{'})\\ \chi_i^*(\boldsymbol{x}_2^{'}) & \chi_j^*(\boldsymbol{x}_2^{'})\end{bmatrix}d\boldsymbol{x}_3\ldots d\boldsymbol{x}_N\ \text{（利用波函数正交性）} \\
&= \frac{1}{2(N-2)!}\sum_{1\le i<j\le N}[\chi_i(\boldsymbol{x}_1)\chi_j(\boldsymbol{x}_2)-\chi_j(\boldsymbol{x}_1)\chi_i(\boldsymbol{x}_2)][\chi_i^*(\boldsymbol{x}_1^{'})\chi_j^*(\boldsymbol{x}_2^{'})-\chi_j^*(\boldsymbol{x}_1^{'})\chi_i^*(\boldsymbol{x}_2^{'})]\cdot(N-2)! \\
&= \frac{1}{2}\sum_{1\le i<j\le N}[\chi_i(\boldsymbol{x}_1)\chi_i^*(\boldsymbol{x}_1^{'})\chi_j(\boldsymbol{x}_2)\chi_j^*(\boldsymbol{x}_2^{'})+\chi_j(\boldsymbol{x}_1)\chi_j^*(\boldsymbol{x}_1^{'})\chi_i(\boldsymbol{x}_2)\chi_i^*(\boldsymbol{x}_2^{'})] \\
&\quad-\frac{1}{2}\sum_{1\le i<j\le N}[\chi_i(\boldsymbol{x}_1)\chi_i^*(\boldsymbol{x}_2^{'})\chi_j(\boldsymbol{x}_2)\chi_j^*(\boldsymbol{x}_1^{'})+\chi_j(\boldsymbol{x}_1)\chi_j^*(\boldsymbol{x}_2^{'})\chi_i(\boldsymbol{x}_2)\chi_i^*(\boldsymbol{x}_1^{'})] \\
&= \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\chi_i(\boldsymbol{x}_1)\chi_i^*(\boldsymbol{x}_1^{'})\chi_j(\boldsymbol{x}_2)\chi_j^*(\boldsymbol{x}_2^{'})-\frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\chi_i(\boldsymbol{x}_1)\chi_i^*(\boldsymbol{x}_2^{'})\chi_j(\boldsymbol{x}_2)\chi_j^*(\boldsymbol{x}_1^{'})\ (i=j\text{时两项抵消}) \\
&= \frac{1}{2}[\gamma_1(\boldsymbol{x}_1;\boldsymbol{x}_1^{'})\gamma_1(\boldsymbol{x}_2;\boldsymbol{x}_2^{'})-\gamma_1(\boldsymbol{x}_1;\boldsymbol{x}_2^{'})\gamma_1(\boldsymbol{x}_2;\boldsymbol{x}_1^{'})]
\end{aligned}
$$

练习3：证明如果一阶约化密度矩阵（算符）可以写成如下形式，则对应的N电子波函数必定是行列式波函数

$$
\gamma_1(\boldsymbol{x}_1;\boldsymbol{x}_1^{'})=\sum_{a=1}^{N}\chi_a(\boldsymbol{x}_1)\chi_a^*(\boldsymbol{x}_1^{'})
$$

$$
\text{or}\quad \hat{\gamma}_1=\sum_{a=1}^{N}|\chi_a\rangle\langle\chi_a|=\sum_i|\chi_i\rangle\langle\chi_i|\quad\left(n_i=\begin{cases}1 & \chi_i\text{ not occupied}\\ 0 & \chi_i\text{ occupied}\end{cases}\right)
$$

证明：给定一组正交归一的单电子轨道$\{\phi_i(\boldsymbol{x}),i=1,2,\ldots\}$，可以由这组单电子轨道构建N电子波函数的行列式基组$\{|\Phi_i\rangle,i=1,2,\ldots\}$，其中$|\Phi_i\rangle=|\phi_{i_1}\phi_{i_2}\ldots\phi_{i_N}\rangle$，

练习4：证明Slater行列式波函数的一阶约化密度矩阵（算符）满足幂等性条件

$$
\begin{cases}\hat{\gamma}_1^2=\hat{\gamma}_1\\ \mathrm{Tr}(\hat{\gamma}_1)=N\end{cases}
$$

证明：由练习2可知Slater行列式波函数的一阶约化密度矩阵满足如下形式：
$\gamma_1(\boldsymbol{x}_1;\boldsymbol{x}_1^{'})=\sum_{a=1}^{N}\chi_a(\boldsymbol{x}_1)\chi_a^*(\boldsymbol{x}_1^{'})$，相应的一阶约化密度算符为$\hat{\gamma}_1=\sum_{a=1}^{N}|\chi_a\rangle\langle\chi_a|$，因此：

$$
\hat{\gamma}_1^2=\sum_{a=1}^{N}|\chi_a\rangle\langle\chi_a|\cdot\sum_{b=1}^{N}|\chi_b\rangle\langle\chi_b|=\sum_{a=1}^{N}\sum_{b=1}^{N}|\chi_a\rangle\langle\chi_b|\delta_{ab}=\sum_{a=1}^{N}|\chi_a\rangle\langle\chi_a|=\hat{\gamma}_1
$$

$$
\mathrm{Tr}(\hat{\gamma}_1)=\int(\boldsymbol{x}|\hat{\gamma}_1|\boldsymbol{x})d\boldsymbol{x}=\int\sum_{a=1}^{N}\chi_a(\boldsymbol{x})\chi_a^*(\boldsymbol{x})d\boldsymbol{x}=N
$$

练习5：证明满足幂等性条件的一阶约化密度矩阵（算符），其对应的N电子波函数必定是行列式波函数

证明：

练习6：写出由$\rho_{\mu\nu} \equiv \int d\boldsymbol{r} \int d\boldsymbol{r}^{'} \phi_{\mu}^{*}(\boldsymbol{r}) \rho_1(\boldsymbol{r}, \boldsymbol{r}^{'}) \phi_{\nu}(\boldsymbol{r}^{'})$构成的矩阵和密度矩阵之间的关系

解：我们知道，对应于RHF基态波函数的无自旋一阶约化密度矩阵可表示为：

$$\rho_1(\boldsymbol{r}, \boldsymbol{r}^{'}) = \sum_{\mu}^{K} \sum_{\nu}^{K} P_{\mu\nu} \phi_{\mu}(\boldsymbol{r}) \phi_{\nu}^{*}(\boldsymbol{r}^{'})$$

因此

$$\rho_{\mu\nu} \equiv \int d\boldsymbol{r} \int d\boldsymbol{r}^{'} \phi_{\mu}^{*}(\boldsymbol{r}) \rho_1(\boldsymbol{r}, \boldsymbol{r}^{'}) \phi_{\nu}(\boldsymbol{r}^{'}) = \int d\boldsymbol{r} \int d\boldsymbol{r}^{'} \phi_{\mu}^{*}(\boldsymbol{r}) [\sum_{\mu^{'}}^{K} \sum_{\nu^{'}}^{K} P_{\mu^{'}\nu^{'}} \phi_{\mu^{'}}(\boldsymbol{r}) \phi_{\nu^{'}}^{*}(\boldsymbol{r}^{'})] \phi_{\nu}(\boldsymbol{r}^{'}) = \sum_{\mu^{'}}^{K} \sum_{\nu^{'}}^{K} S_{\mu\mu^{'}} P_{\mu^{'}\nu^{'}} S_{\nu^{'}\nu}$$

练习7：证明Löwdin有效电荷也可以表示为$\rho_A = 2 \sum_{\mu \in A} \sum_{a}^{\frac{N}{2}} |\langle \phi_{\mu}^{'} | \psi_a \rangle|^2$

证明：由于密度矩阵在Löwdin正交归一化基函数的表示为$\rho(\boldsymbol{r}) = \sum_{\lambda,\eta} P_{\lambda\eta}^{'} \phi_{\lambda}^{'}(\boldsymbol{r}) \phi_{\eta}^{'*}(\boldsymbol{r})$，而$\phi_{\lambda}^{'} = \sum_{\mu} X_{\mu\nu} \phi_{\mu}$，因此

$$\begin{aligned}
\rho_A &= 2 \sum_{\mu \in A} \sum_{a}^{\frac{N}{2}} |\langle \phi_{\mu}^{'} | \psi_a \rangle|^2 = 2 \sum_{\mu \in A} \sum_{a}^{\frac{N}{2}} \langle \psi_a | \phi_{\mu}^{'} \rangle \langle \phi_{\mu}^{'} | \psi_a \rangle = 2 \sum_{\mu \in A} \sum_{a}^{\frac{N}{2}} \sum_{i,j} \langle \phi_j | \phi_{\mu}^{'} \rangle \langle \phi_{\mu}^{'} | \phi_i \rangle C_{ia} C_{ja}^{*} \\
&= 2 \sum_{\mu \in A} \sum_{a}^{\frac{N}{2}} \sum_{i,j} \sum_{k,l} \langle \phi_j | \phi_k \rangle X_{k\mu} X_{l\mu}^{*} \langle \phi_l | \phi_i \rangle C_{ia} C_{ja}^{*} = \sum_{\mu \in A} \sum_{i,j} \sum_{k,l} X_{\mu l}^{\dagger} S_{li} P_{ij} S_{jk} X_{k\mu} \\
&= \sum_{\mu \in A} (\boldsymbol{X}^{\dagger} \boldsymbol{S} \boldsymbol{P} \boldsymbol{S} \boldsymbol{X})_{\mu\mu} = \sum_{\mu \in A} (\boldsymbol{S}^{\frac{1}{2}} \boldsymbol{P} \boldsymbol{S}^{\frac{1}{2}})_{\mu\mu} \text{（利用} \boldsymbol{X}^{\dagger} \boldsymbol{S} \boldsymbol{X} = \boldsymbol{I}\text{，及} \boldsymbol{X} = \boldsymbol{S}^{-\frac{1}{2}}\text{）}
\end{aligned}$$

这与Löwdin有效电荷的定义一致，故证毕

练习8：推导解离极限处氢分子的交换积分为$J_{11} \equiv \langle \psi_1 \psi_1 | \psi_1 \psi_1 \rangle \xrightarrow{R \to \infty} \frac{U}{2}$，其中$U \equiv \iint |\phi_a(\boldsymbol{r}_1)|^2 \frac{1}{r_{12}} |\phi_a(\boldsymbol{r}_2)|^2 d\boldsymbol{r}_1 d\boldsymbol{r}_2$

解：由于解离极限处$R \to \infty$，此时重叠积分$S \equiv \int \phi_a^{*}(\boldsymbol{r}) \phi_b(\boldsymbol{r}) d\boldsymbol{r} \to 0$，相应的波函数为$\psi_1(\boldsymbol{r}) = \frac{\phi_a(\boldsymbol{r}) + \phi_b(\boldsymbol{r})}{\sqrt{2}}$，因此

$$\begin{aligned}
J_{11} &\equiv \langle \psi_1 \psi_1 | \psi_1 \psi_1 \rangle = \iint \psi_1^{*}(\boldsymbol{r}_1) \psi_1^{*}(\boldsymbol{r}_2) \frac{1}{r_{12}} \psi_1(\boldsymbol{r}_1) \psi_1(\boldsymbol{r}_2) d\boldsymbol{r}_1 d\boldsymbol{r}_2 \\
&= \frac{1}{4} \iint \frac{[\phi_a^{*}(\boldsymbol{r}_1) + \phi_b^{*}(\boldsymbol{r}_1)][\phi_a^{*}(\boldsymbol{r}_2) + \phi_b^{*}(\boldsymbol{r}_2)][\phi_a(\boldsymbol{r}_1) + \phi_b(\boldsymbol{r}_1)][\phi_a(\boldsymbol{r}_2) + \phi_b(\boldsymbol{r}_2)]}{r_{12}} d\boldsymbol{r}_1 d\boldsymbol{r}_2 \\
&= \frac{1}{4} \iint \frac{[\phi_a^{*}(\boldsymbol{r}_1)\phi_a(\boldsymbol{r}_1) + \phi_b^{*}(\boldsymbol{r}_1)\phi_b(\boldsymbol{r}_1)][\phi_a^{*}(\boldsymbol{r}_2)\phi_a(\boldsymbol{r}_2) + \phi_b^{*}(\boldsymbol{r}_2)\phi_b(\boldsymbol{r}_2)]}{r_{12}} d\boldsymbol{r}_1 d\boldsymbol{r}_2 \text{（利用重叠积分为}0\text{的性质）} \\
&= \frac{1}{4} \iint \frac{\phi_a^{*}(\boldsymbol{r}_1)\phi_a^{*}(\boldsymbol{r}_2)\phi_a(\boldsymbol{r}_1)\phi_a(\boldsymbol{r}_2) + \phi_b^{*}(\boldsymbol{r}_1)\phi_b^{*}(\boldsymbol{r}_2)\phi_b(\boldsymbol{r}_1)\phi_b(\boldsymbol{r}_2)}{r_{12}} d\boldsymbol{r}_1 d\boldsymbol{r}_2 \text{（利用轨道不同的电子间距无穷远时积分项为}0\text{）} \\
&= \frac{U}{2}
\end{aligned}$$

从而原题得证

练习4.5

1.写出解离极限时的UHF基态波函数

解：解离极限时的UHF基态波函数为$|\phi_a\bar{\phi}_b\rangle = \frac{1}{\sqrt{2!}}\begin{vmatrix} \phi_a(\boldsymbol{r}_1) & \bar{\phi}_b(\boldsymbol{r}_1) \\ \phi_a(\boldsymbol{r}_2) & \bar{\phi}_b(\boldsymbol{r}_2) \end{vmatrix}$

2.解离极限时UHF行列式波函数对应的$\hat{S}^2$的期望值是多少?

解：由于解离极限时的UHF基态波函数为$|\phi_a\bar{\phi}_b\rangle$，其重叠积分为0，$N_\beta = 1$，$N_\alpha - N_\beta = 0$，因此$\langle\hat{S}^2\rangle_{\text{exact}} = 0$，根据自旋污染的表达式$\langle\hat{S}^2\rangle_{\text{UHF}} = \langle\hat{S}^2\rangle_{\text{exact}} + N_\beta - \sum_{i=1}^{N_\alpha}\sum_{j=1}^{N_\beta}|S_{ij}^{\alpha\beta}|^2$，我们有$\langle\hat{S}^2\rangle_{\text{UHF}} = N_\beta = 1$