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$|\chi_1 \ldots \chi_N\rangle$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

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

结合Slater行列式波函数的含义

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

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

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

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}\operatorname{cof}\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}\operatorname{cof}\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\operatorname{cof}\begin{bmatrix}\chi_i(\boldsymbol{x}_1) & \chi_j(\boldsymbol{x}_1)\\ \chi_i(\boldsymbol{x}_2) & \chi_j(\boldsymbol{x}_2)\end{bmatrix}\operatorname{cof}\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')\text{（}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

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

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

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$|\Phi_i\rangle=|\phi_{i_1}\phi_{i_2}\ldots\phi_{i_N}\rangle$，对于任意一个N电子波函数，总可以用这个行列式基组展开：$|\Phi\rangle=\sum_{i=1}^{\infty}C_i|\Phi_i\rangle$（之所以采用Slater行列式作为基组并展开，是因为Slater行列式满足交换反对称性），其密度算符为$\hat{\gamma}=|\Phi\rangle\langle\Phi|=\sum_{i,j=1}^{\infty}C_iC_j^*|\Phi_i\rangle\langle\Phi_j|$，因此其一阶约化密度矩阵可写作如下形式：

$$
\gamma_1^{|\Phi\rangle}(\boldsymbol{x}_1;\boldsymbol{x}_1')=\sum_{i,j=1}^{\infty}C_iC_j^*\gamma_1^{ij}(\boldsymbol{x}_1;\boldsymbol{x}_1')=\sum_{i,j=1}^{\infty}C_iC_j^*N\int\cdots\int(\boldsymbol{x}_1,\boldsymbol{x}_2,\ldots,\boldsymbol{x}_N|\Phi_i\rangle\langle\Phi_j|\boldsymbol{x}_1',\boldsymbol{x}_2,\ldots,\boldsymbol{x}_N)d\boldsymbol{x}_2d\boldsymbol{x}_3\ldots d\boldsymbol{x}_N
$$

根据单电子轨道$\phi_i(\boldsymbol{x})$正交归一的性质，我们有如下引理：$\gamma_1^{ij}(\boldsymbol{x}_1;\boldsymbol{x}_1')$不为零当且仅当$|\Phi_i\rangle$与$|\Phi_j\rangle$所包含的单电子轨道最多只有一个不相同，且若$|\Phi_i\rangle$与$|\Phi_j\rangle$所包含的单电子轨道有一个不相同（即$|\Phi_i\rangle$与$|\Phi_j\rangle$均包含$\phi_{l_1},\phi_{l_2},\ldots,\phi_{l_{N-1}}$，但$|\Phi_i\rangle$包含$\phi_m$，而$|\Phi_j\rangle$包含$\phi_n$），则存在如下变换，使得$|\Phi_i\rangle$与$|\Phi_j\rangle$相互对齐：$|\Phi_i\rangle\to|\phi_m\phi_{l_1}\phi_{l_2}\ldots\phi_{l_{N-1}}\rangle$，$|\Phi_j\rangle\to|\phi_n\phi_{l_1}\phi_{l_2}\ldots\phi_{l_{N-1}}\rangle$。记这样的操作需要的交换次数之和为$\mathcal{P}_{ij}$，则

$$
\begin{aligned}
\gamma_1^{ij}(\boldsymbol{x}_1;\boldsymbol{x}_1') &= (-1)^{\mathcal{P}_{ij}} N \int\cdots\int \Phi_i'(\boldsymbol{x}_1,\boldsymbol{x}_2,\ldots,\boldsymbol{x}_N)\Phi_j'^{*}(\boldsymbol{x}_1',\boldsymbol{x}_2,\ldots,\boldsymbol{x}_N)d\boldsymbol{x}_2 d\boldsymbol{x}_3\ldots d\boldsymbol{x}_N \\
&= (-1)^{\mathcal{P}_{ij}} N \int\cdots\int \frac{1}{\sqrt{N!}}\left\{\phi_m(\boldsymbol{x}_1)\mathrm{cof}[\phi_m(\boldsymbol{x}_1)] + \sum_{i=1}^{N-1}(-1)^{2+i}\phi_{l_i}(\boldsymbol{x}_1)\mathrm{cof}[\phi_{l_i}(\boldsymbol{x}_1)]\right\} \\
&\quad \cdot \frac{1}{\sqrt{N!}}\left\{\phi_n^*(\boldsymbol{x}_1')\mathrm{cof}[\phi_n^*(\boldsymbol{x}_1')] + \sum_{j=2}^{N}(-1)^{2+j}\phi_{l_j}^*(\boldsymbol{x}_1')\mathrm{cof}[\phi_{l_j}^*(\boldsymbol{x}_1')]\right\}d\boldsymbol{x}_2 d\boldsymbol{x}_3\ldots d\boldsymbol{x}_N \\
&= (-1)^{\mathcal{P}_{ij}}\frac{1}{(N-1)!}\int\cdots\int \phi_m(\boldsymbol{x}_1)\phi_n^*(\boldsymbol{x}_1')\mathrm{cof}[\phi_m(\boldsymbol{x}_1)]\mathrm{cof}[\phi_n^*(\boldsymbol{x}_1')]d\boldsymbol{x}_2 d\boldsymbol{x}_3\ldots d\boldsymbol{x}_N \text{（利用正交性）} \\
&= (-1)^{\mathcal{P}_{ij}}\phi_m(\boldsymbol{x}_1)\phi_n^*(\boldsymbol{x}_1')
\end{aligned}
$$

若$|\Phi_i\rangle$与$|\Phi_j\rangle$所包含的单电子轨道完全相同，则如练习2所示，有$\gamma_1^{ii}(\boldsymbol{x}_1;\boldsymbol{x}_1') = \sum\limits_{a=1}^{N}\phi_{i_a}(\boldsymbol{x}_1)\phi_{i_a}^*(\boldsymbol{x}_1')$，从而我们可以把任意一个N电子波函数的一阶约化密度矩阵写成如下形式（connected表示$|\Phi_i\rangle$与$|\Phi_j\rangle$只相差一个单电子轨道，下标分别为m_{ij}和n_{ij}）：

$$
\gamma_1^{|\Phi\rangle}(\boldsymbol{x}_1;\boldsymbol{x}_1') = \sum_{i=1}^{\infty}|C_i|^2\sum_{a=1}^{N}\phi_{i_a}(\boldsymbol{x}_1)\phi_{i_a}^*(\boldsymbol{x}_1') + \sum_{i\neq j,\ \mathrm{connected}}^{\infty} C_iC_j^*(-1)^{\mathcal{P}_{ij}}\phi_{m_{ij}}(\boldsymbol{x}_1)\phi_{n_{ij}}^*(\boldsymbol{x}_1')
$$

注意到$\{\phi_i(\boldsymbol{x}_1)\phi_j^*(\boldsymbol{x}_1'), i,j=1,2,\ldots\}$作为一组正交归一的双电子基组，可用来展开任意单电子算符在坐标表象的矩阵表示，且展开式唯一，即：

$$
\langle\boldsymbol{x}_1|\hat{O}|\boldsymbol{x}_1'\rangle = \sum_{i,j}\langle\boldsymbol{x}_1|\phi_i\rangle\langle\phi_i|\hat{O}|\phi_j\rangle\langle\phi_j|\boldsymbol{x}_1'\rangle = \sum_{i,j}O_{ij}\phi_i(\boldsymbol{x}_1)\phi_j^*(\boldsymbol{x}_1')
$$

现在我们将题中条件的单电子轨道$\{\chi_i(\boldsymbol{x}), i=1,2,\ldots\}$包括在$\{\phi_i(\boldsymbol{x}), i=1,2,\ldots\}$中，并对比题目中的等式与上面写出的一阶约化密度矩阵表达式，假设态矢$|\Phi\rangle$的展开式中至少有两个行列式的系数不为0，则上面写出的一阶约化密度矩阵表达式中，右边第一项至少有$(N+1)$个形如$\phi_l(\boldsymbol{x}_1)\phi_l^*(\boldsymbol{x}_1')$的双电子基函数前的系数不为0，这与题目中的等式矛盾。故假设错误，态矢$|\Phi\rangle$的展开式中只有一个行列式的系数不为0，即该波函数本身就是行列式波函数。

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：
$\gamma_1(\boldsymbol{x}_1;\boldsymbol{x}_1') = \sum\limits_{a=1}^{N}\chi_a(\boldsymbol{x}_1)\chi_a^*(\boldsymbol{x}_1')$，相应的一阶约化密度算符为$\hat{\gamma}_1 = \sum\limits_{a=1}^{N}|\chi_a\rangle\langle\chi_a|$，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：仍然按练习3的假设，构造出一个用行列式基组展开的N电子波函数$|\Phi\rangle = \sum\limits_{i=1}^{\infty}C_i|\Phi_i\rangle$，其密度算符为$\hat{\gamma} = |\Phi\rangle\langle\Phi| = \sum\limits_{i,j=1}^{\infty}C_iC_j^*|\Phi_i\rangle\langle\Phi_j|$，而相应的一阶约化密度矩阵为：

$$
\gamma_1^{|\Phi\rangle}(\boldsymbol{x}_1;\boldsymbol{x}_1') = \sum_{i=1}^{\infty}|C_i|^2\sum_{a=1}^{N}\phi_{i_a}(\boldsymbol{x}_1)\phi_{i_a}^*(\boldsymbol{x}_1') + \sum_{i\neq j,\ \mathrm{connected}}^{\infty} C_iC_j^*(-1)^{\mathcal{P}_{ij}}\phi_{m_{ij}}(\boldsymbol{x}_1)\phi_{n_{ij}}^*(\boldsymbol{x}_1')
$$

从而对应的一阶约化密度算符为：

$$\hat{\gamma}_1^{|\Phi\rangle}=\sum_{i=1}^{\infty}|C_i|^2\sum_{a=1}^{N}|\phi_{i_a}\rangle\langle\phi_{i_a}|+\sum_{i\neq j,\ \text{connected}}^{\infty}C_iC_j^*(-1)^{\mathcal{P}_{ij}}|\phi_{m_{ij}}\rangle\langle\phi_{n_{ij}}|$$

如果所有行列式基组之间均存在至少有两个不相同的单电子轨道，那么$\hat{\gamma}_1^{|\Phi\rangle}=\sum_{i=1}^{\infty}|C_i|^2\sum_{a=1}^{N}|\phi_{i_a}\rangle\langle\phi_{i_a}|$，从而有：

$$\begin{aligned}(\hat{\gamma}_1^{|\Phi\rangle})^2&=\sum_{i=1}^{\infty}|C_i|^2\sum_{a=1}^{N}|\phi_{i_a}\rangle\langle\phi_{i_a}|\cdot\sum_{j=1}^{\infty}|C_j|^2\sum_{b=1}^{N}|\phi_{j_b}\rangle\langle\phi_{j_b}|=\sum_{i,j=1}^{\infty}|C_i|^2|C_j|^2\sum_{a,b=1}^{N}|\phi_{i_a}\rangle\langle\phi_{i_a}|\phi_{j_b}\rangle\langle\phi_{j_b}|\\&=\sum_{i,j=1}^{\infty}|C_i|^2|C_j|^2\sum_{a,b=1}^{N}\delta_{i_a,j_b}|\phi_{i_a}\rangle\langle\phi_{j_b}|=\sum_{i=1}^{\infty}|C_i|^4\sum_{a=1}^{N}|\phi_{i_a}\rangle\langle\phi_{i_a}|+\sum_{i\neq j}^{\infty}|C_i|^2|C_j|^2\sum_{a,b=1}^{N}\delta_{i_a,j_b}|\phi_{i_a}\rangle\langle\phi_{j_b}|\end{aligned}$$

根据幂等性的条件，我们有：

$$\begin{cases}|C_i|^4=|C_i|^2\ \text{and}\ |C_i|^2|C_j|^2=0\ (i\neq j)\\ \text{Tr}(\hat{\gamma}_1^{|\Phi\rangle})=\sum_{i=1}^{\infty}|C_i|^2\sum_{a=1}^{N}\langle\boldsymbol{x}|\phi_{i_a}\rangle\langle\phi_{i_a}|\boldsymbol{x}\rangle=N\sum_{i=1}^{\infty}|C_i|^2=N\end{cases}$$

由以上方程组可知，只能有一个$|C_i|^2=1$，其余的$|C_i|^2$只能取零，于是对应的N电子波函数即为行列式波函数。
如果存在至少一对行列式基组，它们之间不相同的单电子轨道只有一个，那么有（为了书写方便，"connected"简写为"con"）：

$$\begin{aligned}(\hat{\gamma}_1^{|\Phi\rangle})^2&=(\sum_{i=1}^{\infty}|C_i|^2\sum_{a=1}^{N}|\phi_{i_a}\rangle\langle\phi_{i_a}|+\sum_{i\neq j,\ \text{con}}^{\infty}C_iC_j^*(-1)^{\mathcal{P}_{ij}}|\phi_{m_{ij}}\rangle\langle\phi_{n_{ij}}|)\cdot(\sum_{k=1}^{\infty}|C_k|^2\sum_{b=1}^{N}|\phi_{k_b}\rangle\langle\phi_{k_b}|+\sum_{k\neq l,\ \text{con}}^{\infty}C_kC_l^*(-1)^{\mathcal{P}_{kl}}|\phi_{m_{kl}}\rangle\langle\phi_{n_{kl}}|)\\&=\sum_{i=1}^{\infty}|C_i|^4\sum_{a=1}^{N}|\phi_{i_a}\rangle\langle\phi_{i_a}|+\sum_{i\neq j}^{\infty}|C_i|^2|C_j|^2\sum_{a,b=1}^{N}\delta_{i_a,j_b}|\phi_{i_a}\rangle\langle\phi_{j_b}|+\sum_{i\neq j,\ \text{con}}^{\infty}\sum_{k\neq l,\ \text{con}}^{\infty}C_iC_j^*C_kC_l^*(-1)^{\mathcal{P}_{ij}+\mathcal{P}_{kl}}\delta_{n_{ij},m_{kl}}|\phi_{m_{ij}}\rangle\langle\phi_{n_{kl}}|+\text{etc.}\\&=\sum_{i=1}^{\infty}|C_i|^4\sum_{a=1}^{N}|\phi_{i_a}\rangle\langle\phi_{i_a}|+\sum_{i\neq j}^{\infty}|C_i|^2|C_j|^2\sum_{a,b=1}^{N}\delta_{i_a,j_b}|\phi_{i_a}\rangle\langle\phi_{j_b}|+\sum_{i\neq j,j\neq l,\text{con}}^{\infty}C_iC_l^*|C_j|^2(-1)^{\mathcal{P}_{ij}+\mathcal{P}_{jl}}|\phi_{m_{ij}}\rangle\langle\phi_{n_{jl}}|+\text{etc.}\end{aligned}$$

上式中的$\mathcal{P}_{ij}+\mathcal{P}_{jl}$相当于利用交换波函数排列顺序，从行列式波函数$|\Phi_i\rangle$变换到$|\Phi_j\rangle$再变换到$|\Phi_l\rangle$的次数，其等于$\mathcal{P}_{il}$，从而根据幂等性的条件，我们仍然有：

$$\begin{cases}|C_i|^4=|C_i|^2\ \text{and}\ |C_i|^2|C_j|^2=0\ (i\neq j)\\ \sum_{i\neq j,j\neq l,\text{con}}^{\infty}C_iC_l^*|C_j|^2(-1)^{\mathcal{P}_{il}}|\phi_{m_{ij}}\rangle\langle\phi_{n_{jl}}|=\sum_{i\neq l,\text{con}}^{\infty}C_iC_l^*(-1)^{\mathcal{P}_{il}}|\phi_{m_{il}}\rangle\langle\phi_{n_{il}}|\\ \text{Tr}(\hat{\gamma}_1^{|\Phi\rangle})=\sum_{i=1}^{\infty}|C_i|^2\sum_{a=1}^{N}\langle\boldsymbol{x}|\phi_{i_a}\rangle\langle\phi_{i_a}|\boldsymbol{x}\rangle=N\sum_{i=1}^{\infty}|C_i|^2=N\end{cases}$$

由以上方程组可知，同样只能有一个$|C_i|^2=1$，其余的$|C_i|^2$只能取零，于是对应的N电子波函数即为行列式波函数（这一部分的证明不算非常严谨，但大致表明了原因）。综上，原题得证。

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

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

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

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

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 $\langle \hat{S}^2 \rangle_{\text{UHF}} = N_\beta = 1$