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$\chi_i(\boldsymbol{x}_1)$后的代数余子式，我们有：

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

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}\text{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}\text{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\text{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}\text{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')\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

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

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

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：$|\Phi\rangle=\sum\limits_{i=1}^{\infty}C_i|\Phi_i\rangle$（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$\hat{\gamma}=|\Phi\rangle\langle\Phi|=\sum\limits_{i,j=1}^{\infty}C_iC_j^*|\Phi_i\rangle\langle\Phi_j|$，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

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

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$\gamma_1^{ii}(\boldsymbol{x}_1;\boldsymbol{x}_1') = \sum_{a=1}^{N}\phi_{i_a}(\boldsymbol{x}_1)\phi_{i_a}^*(\boldsymbol{x}_1')$，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}）：

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

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

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

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$U\equiv\iint|\phi_a(\boldsymbol{r}_1)|^2\frac{1}{r_{12}}|\phi_a(\boldsymbol{r}_2)|^2d\boldsymbol{r}_1d\boldsymbol{r}_2$

解：由于解离极限处$R\to\infty$，此时重叠积分$S\equiv\int\phi_a^*(\boldsymbol{r})\phi_b(\boldsymbol{r})d\boldsymbol{r}\to0$，相应的波函数为$\psi_1(\boldsymbol{r})=\frac{\phi_a(\boldsymbol{r})+\phi_b(\boldsymbol{r})}{\sqrt{2}}$，因此

$$\begin{aligned}J_{11}&\equiv\langle\psi_1\psi_1|\psi_1\psi_1\rangle=\iint\psi_1^*(\boldsymbol{r}_1)\psi_1^*(\boldsymbol{r}_2)\frac{1}{r_{12}}\psi_1(\boldsymbol{r}_1)\psi_1(\boldsymbol{r}_2)d\boldsymbol{r}_1d\boldsymbol{r}_2\\&=\frac{1}{4}\iint\frac{[\phi_a^*(\boldsymbol{r}_1)+\phi_b^*(\boldsymbol{r}_1)][\phi_a^*(\boldsymbol{r}_2)+\phi_b^*(\boldsymbol{r}_2)][\phi_a(\boldsymbol{r}_1)+\phi_b(\boldsymbol{r}_1)][\phi_a(\boldsymbol{r}_2)+\phi_b(\boldsymbol{r}_2)]}{r_{12}}d\boldsymbol{r}_1d\boldsymbol{r}_2\\&=\frac{1}{4}\iint\frac{[\phi_a^*(\boldsymbol{r}_1)\phi_a(\boldsymbol{r}_1)+\phi_b^*(\boldsymbol{r}_1)\phi_b(\boldsymbol{r}_1)][\phi_a^*(\boldsymbol{r}_2)\phi_a(\boldsymbol{r}_2)+\phi_b^*(\boldsymbol{r}_2)\phi_b(\boldsymbol{r}_2)]}{r_{12}}d\boldsymbol{r}_1d\boldsymbol{r}_2\text{（利用重叠积分为0的性质）}\\&=\frac{1}{4}\iint\frac{\phi_a^*(\boldsymbol{r}_1)\phi_a^*(\boldsymbol{r}_2)\phi_a(\boldsymbol{r}_1)\phi_a(\boldsymbol{r}_2)+\phi_b^*(\boldsymbol{r}_1)\phi_b^*(\boldsymbol{r}_2)\phi_b(\boldsymbol{r}_1)\phi_b(\boldsymbol{r}_2)}{r_{12}}d\boldsymbol{r}_1d\boldsymbol{r}_2\text{（利用轨道不同的电子间距无穷远时积分项为0）}\\&=\frac{U}{2}\end{aligned}$$

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