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

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

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：

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

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{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}\operatorname{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\operatorname{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}\operatorname{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：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

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

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

练习4：证明Slater行列式波函数的一阶约化密度矩阵（矩阵）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：

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：

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：

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：

练习4.5

1.写出解离极限时的UHF基态波函数

2.解离极限时UHF行列式波函数对应的的期望值是多少?