课堂练习

练习1：证明对于混合态的密度算符不具备幂等性，即$\hat{\Gamma}^2 \neq \hat{\Gamma}$

证明：由于$\hat{\Gamma} = \sum_i p_i |\Psi_i\rangle\langle\Psi_i|$，其中$0 \leq p_i \leq 1$，$\sum_i p_i = 1$，因此

$$\hat{\Gamma}^2 \equiv \hat{\Gamma} \cdot \hat{\Gamma} = \sum_i p_i |\Psi_i\rangle\langle\Psi_i| \cdot \sum_j p_j |\Psi_j\rangle\langle\Psi_j| = \sum_i \sum_j p_i p_j |\Psi_i\rangle\langle\Psi_i|\Psi_j\rangle\langle\Psi_j|$$

从而有

$$\mathrm{Tr}(\hat{\Gamma}) = \int (\boldsymbol{x}^N|\hat{\Gamma}|\boldsymbol{x}^N) d\boldsymbol{x}^N = \int (\boldsymbol{x}^N| \sum_i p_i |\Psi_i\rangle\langle\Psi_i| \cdot |\boldsymbol{x}^N) d\boldsymbol{x}^N = \int \sum_i p_i (\boldsymbol{x}^N|\Psi_i\rangle\langle\Psi_i|\boldsymbol{x}^N) d\boldsymbol{x}^N = \sum_i p_i = 1$$

$$\begin{aligned}
\mathrm{Tr}(\hat{\Gamma}^2) &= \int (\boldsymbol{x}^N|\hat{\Gamma}^2|\boldsymbol{x}^N) d\boldsymbol{x}^N = \int (\boldsymbol{x}^N| \sum_i p_i |\Psi_i\rangle\langle\Psi_i| \cdot \sum_j p_j |\Psi_j\rangle\langle\Psi_j||\boldsymbol{x}^N) d\boldsymbol{x}^N = \int \sum_i \sum_j p_i p_j (\boldsymbol{x}^N|\Psi_i\rangle\langle\Psi_i|\Psi_j\rangle\langle\Psi_j|\boldsymbol{x}^N) d\boldsymbol{x}^N \\
&= \int \sum_i \sum_j p_i p_j \langle\Psi_j|\boldsymbol{x}^N)(\boldsymbol{x}^N|\Psi_i\rangle\langle\Psi_i|\Psi_j\rangle d\boldsymbol{x}^N = \sum_i \sum_j p_i p_j \langle\Psi_j|\Psi_i\rangle\langle\Psi_i|\Psi_j\rangle = \sum_i p_i (\sum_j p_j \langle\Psi_j|\Psi_i\rangle\langle\Psi_i|\Psi_j\rangle) \\
&< \sum_i p_i (\sum_j p_j \langle\Psi_i|\Psi_i\rangle\langle\Psi_j|\Psi_j\rangle) = \sum_i p_i (\sum_j p_j) = \sum_i p_i \cdot 1 = 1 \cdot 1 = 1 = \mathrm{Tr}(\hat{\Gamma})
\end{aligned}$$

此处利用到$|\Psi_i\rangle \neq |\Psi_j\rangle$，$\langle\Psi_i|\Psi_i\rangle = \langle\Psi_j|\Psi_j\rangle = 1$，因此$\mathrm{Tr}(\hat{\Gamma}^2) \neq \mathrm{Tr}(\hat{\Gamma})$，从而$\hat{\Gamma}^2 \neq \hat{\Gamma}$，证毕

练习2：写出从二阶约化密度矩阵计算一阶约化密度矩阵的公式

解：由于一阶约化密度矩阵为

$$\gamma_1(\boldsymbol{x}_1'; \boldsymbol{x}_1) = N \int \cdots \int \gamma_N(\boldsymbol{x}_1', \boldsymbol{x}_2', \ldots, \boldsymbol{x}_N'; \boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N) d\boldsymbol{x}_2 \ldots d\boldsymbol{x}_N$$

二阶约化密度矩阵为

$$\gamma_2(\boldsymbol{x}_1', \boldsymbol{x}_2'; \boldsymbol{x}_1, \boldsymbol{x}_2) = \frac{N(N-1)}{2} \int \cdots \int \gamma_N(\boldsymbol{x}_1', \boldsymbol{x}_2', \ldots, \boldsymbol{x}_N'; \boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N) d\boldsymbol{x}_3 \ldots d\boldsymbol{x}_N$$

因此代入得

$$\begin{aligned}
\gamma_1(\boldsymbol{x}_1'; \boldsymbol{x}_1) &= N \int [\int \cdots \int \gamma_N(\boldsymbol{x}_1', \boldsymbol{x}_2', \ldots, \boldsymbol{x}_N'; \boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N) \ldots d\boldsymbol{x}_N] d\boldsymbol{x}_2 \\
&= N \int \frac{2}{N(N-1)} \gamma_2(\boldsymbol{x}_1', \boldsymbol{x}_2'; \boldsymbol{x}_1, \boldsymbol{x}_2) d\boldsymbol{x}_2 = \frac{2}{N-1} \int \gamma_2(\boldsymbol{x}_1', \boldsymbol{x}_2'; \boldsymbol{x}_1, \boldsymbol{x}_2) d\boldsymbol{x}_2
\end{aligned}$$

练习3：请问一阶约化矩阵（或算符）是否满足幂等性，为什么？

解：一阶约化矩阵（或算符）不一定满足幂等性，因为根据一阶约化密度矩阵的算符形式
$\hat{\gamma}_1 = \sum_i n_i |\psi_i\rangle\langle\psi_i|$，我们有

$$\hat{\gamma}_1^2 = \hat{\gamma}_1 \cdot \hat{\gamma}_1 = \sum_i n_i |\psi_i\rangle\langle\psi_i| \cdot \sum_j n_j |\psi_j\rangle\langle\psi_j| = \sum_i \sum_j n_i n_j |\psi_i\rangle\langle\psi_i|\psi_j\rangle\langle\psi_j| = \sum_i \sum_j n_i n_j \delta_{ij} |\psi_i\rangle\langle\psi_j| = \sum_i n_i^2 |\psi_i\rangle\langle\psi_i|$$

若$n_i \in (0, 1)$，则有$n_i^2 < n_i$，因此$\hat{\gamma}_1^2 = \sum_i n_i^2 |\psi_i\rangle\langle\psi_i| < \sum_i n_i |\psi_i\rangle\langle\psi_i| = \hat{\gamma}_1$，即一阶约化矩阵（或算符）不一定满足幂等性。当且仅当$n_i = 0$或$n_i = 1$时，一阶约化矩阵（或算符）才能满足幂等性。

练习4：证明Fock算符是个厄米算符

证明：我们记

$$h_{ij}=\langle\chi_i(\boldsymbol{x}_1)|\hat{h}(\boldsymbol{x}_1)|\chi_j(\boldsymbol{x}_1)\rangle=\int\chi_i^*(\boldsymbol{x}_1)\hat{h}(\boldsymbol{r}_1)\chi_j(\boldsymbol{x}_1)d\boldsymbol{x}$$

$$\langle\chi_i(\boldsymbol{x}_1)|\hat{J}_k(\boldsymbol{x}_1)|\chi_j(\boldsymbol{x}_1)\rangle\equiv\langle ik|jk\rangle=\int d\boldsymbol{x}_1\int d\boldsymbol{x}_2\chi_i^*(\boldsymbol{x}_1)\chi_k^*(\boldsymbol{x}_2)\boldsymbol{r}_{12}^{-1}\chi_j(\boldsymbol{x}_1)\chi_k(\boldsymbol{x}_2)$$

$$\langle\chi_i(\boldsymbol{x}_1)|\hat{K}_k(\boldsymbol{x}_1)|\chi_j(\boldsymbol{x}_1)\rangle\equiv\langle ik|kj\rangle=\int d\boldsymbol{x}_1\int d\boldsymbol{x}_2\chi_i^*(\boldsymbol{x}_1)\chi_k^*(\boldsymbol{x}_2)\boldsymbol{r}_{12}^{-1}\chi_k(\boldsymbol{x}_1)\chi_j(\boldsymbol{x}_2)$$

则对于Fock算符$\hat{f}(\boldsymbol{x}_1)=\hat{h}(\boldsymbol{x}_1)+\sum_b^N[\hat{J}_b(\boldsymbol{x}_1)-\hat{K}_b(\boldsymbol{x}_1)]$，有

$$f_{ij}=\langle\chi_i(\boldsymbol{x}_1)|\hat{f}(\boldsymbol{x}_1)|\chi_j(\boldsymbol{x}_1)\rangle=h_{ij}+\sum_b(\langle ib|jb\rangle-\langle ib|bj\rangle)$$

$$\begin{aligned}f_{ij}^*&=\langle\chi_i(\boldsymbol{x}_1)|\hat{f}(\boldsymbol{x}_1)|\chi_j(\boldsymbol{x}_1)\rangle^*=h_{ij}^*+\sum_b(\langle ib|jb\rangle^*-\langle ib|bj\rangle^*)=h_{ji}+\sum_b(\langle jb|ib\rangle-\langle bj|ib\rangle)\\&=h_{ji}+\sum_b(\langle jb|ib\rangle-\langle jb|bi\rangle)=f_{ji}\end{aligned}$$

综上，Fock算符是个厄米算符，证毕

练习5：证明行列式波函数满足幺正变换不变性：即对构成行列式波函数$|\Phi\rangle=|\chi_1\dots\chi_N\rangle$的单电子轨道作幺正变化，$\widetilde{\chi}_\mu=\sum_\nu U_{\mu\nu}^*\chi_\nu$，行列式波函数保持不变，$|\Phi\rangle=|\widetilde{\chi}_1\dots\widetilde{\chi}_N\rangle$。

证明：将两个Slater行列式展开，得：

$$|\chi_1\dots\chi_N\rangle=\frac{1}{\sqrt{N!}}\begin{vmatrix}\chi_1(\boldsymbol{x}_1)&\chi_2(\boldsymbol{x}_1)&\dots&\chi_N(\boldsymbol{x}_1)\\\chi_1(\boldsymbol{x}_2)&\chi_2(\boldsymbol{x}_2)&\dots&\chi_N(\boldsymbol{x}_2)\\\vdots&\vdots&\ddots&\vdots\\\chi_1(\boldsymbol{x}_N)&\chi_2(\boldsymbol{x}_N)&\dots&\chi_N(\boldsymbol{x}_N)\end{vmatrix}$$

$$|\widetilde{\chi}_1\dots\widetilde{\chi}_N\rangle=\frac{1}{\sqrt{N!}}\begin{vmatrix}\widetilde{\chi}_1(\boldsymbol{x}_1)&\widetilde{\chi}_2(\boldsymbol{x}_1)&\dots&\widetilde{\chi}_N(\boldsymbol{x}_1)\\\widetilde{\chi}_1(\boldsymbol{x}_2)&\widetilde{\chi}_2(\boldsymbol{x}_2)&\dots&\widetilde{\chi}_N(\boldsymbol{x}_2)\\\vdots&\vdots&\ddots&\vdots\\\widetilde{\chi}_1(\boldsymbol{x}_N)&\widetilde{\chi}_2(\boldsymbol{x}_N)&\dots&\widetilde{\chi}_N(\boldsymbol{x}_N)\end{vmatrix}=\frac{1}{\sqrt{N!}}\begin{vmatrix}\sum_i U_{1i}^*\chi_i(\boldsymbol{x}_1)&\sum_i U_{2i}^*\chi_i(\boldsymbol{x}_1)&\dots&\sum_i U_{Ni}^*\chi_N(\boldsymbol{x}_1)\\\sum_i U_{1i}^*\chi_i(\boldsymbol{x}_2)&\sum_i U_{2i}^*\chi_i(\boldsymbol{x}_2)&\dots&\sum_i U_{Ni}^*\chi_N(\boldsymbol{x}_2)\\\vdots&\vdots&\ddots&\vdots\\\sum_i U_{1i}^*\chi_1(\boldsymbol{x}_N)&\sum_i U_{2i}^*\chi_2(\boldsymbol{x}_N)&\dots&\sum_i U_{Ni}^*\chi_N(\boldsymbol{x}_N)\end{vmatrix}$$

观察这两个式子，我们发现它与如下矩阵相乘的等式有关：

$$\begin{bmatrix}\sum_i U_{1i}^*\chi_i(\boldsymbol{x}_1)&\sum_i U_{2i}^*\chi_i(\boldsymbol{x}_1)&\dots&\sum_i U_{Ni}^*\chi_N(\boldsymbol{x}_1)\\\sum_i U_{1i}^*\chi_i(\boldsymbol{x}_2)&\sum_i U_{2i}^*\chi_i(\boldsymbol{x}_2)&\dots&\sum_i U_{Ni}^*\chi_N(\boldsymbol{x}_2)\\\vdots&\vdots&\ddots&\vdots\\\sum_i U_{1i}^*\chi_1(\boldsymbol{x}_N)&\sum_i U_{2i}^*\chi_2(\boldsymbol{x}_N)&\dots&\sum_i U_{Ni}^*\chi_N(\boldsymbol{x}_N)\end{bmatrix}=\begin{bmatrix}\chi_1(\boldsymbol{x}_1)&\chi_2(\boldsymbol{x}_1)&\dots&\chi_N(\boldsymbol{x}_1)\\\chi_1(\boldsymbol{x}_2)&\chi_2(\boldsymbol{x}_2)&\dots&\chi_N(\boldsymbol{x}_2)\\\vdots&\vdots&\ddots&\vdots\\\chi_1(\boldsymbol{x}_N)&\chi_2(\boldsymbol{x}_N)&\dots&\chi_N(\boldsymbol{x}_N)\end{bmatrix}\begin{bmatrix}U_{11}^*&U_{21}^*&\dots&U_{N1}^*\\U_{12}^*&U_{22}^*&\dots&U_{N2}^*\\\vdots&\vdots&\ddots&\vdots\\U_{1N}^*&U_{2N}^*&\dots&U_{NN}^*\end{bmatrix}$$

根据行列式的性质（若$\mathbf{A},\mathbf{B}$均为n级矩阵，则$|\mathbf{AB}|=|\mathbf{A}||\mathbf{B}|$），我们有

$|\widetilde{\chi}_1\dots\widetilde{\chi}_N\rangle=|\chi_1\dots\chi_N\rangle\cdot|\mathbf{U}^\dagger|$，其中$|\mathbf{U}^\dagger|=\begin{vmatrix} U_{11}^* & U_{21}^* & \dots & U_{N1}^* \\ U_{12}^* & U_{22}^* & \dots & U_{N2}^* \\ \vdots & \vdots & \ddots & \vdots \\ U_{1N}^* & U_{2N}^* & \dots & U_{NN}^* \end{vmatrix}$，为幺正矩阵$\mathbf{U}^\dagger$对应的行列式，而幺正矩阵满足$\mathbf{U}^\dagger\mathbf{U}=\mathbf{U}\mathbf{U}^\dagger=\mathbf{I}$，因此$|\mathbf{U}^\dagger||\mathbf{U}|=|\mathbf{U}^\dagger\mathbf{U}|=|\mathbf{I}|=1$，另一方面，由于$|\mathbf{U}^\dagger|=|\mathbf{U}|^*$，因此有$|\mathbf{U}^\dagger||\mathbf{U}|=|\mathbf{U}|^*|\mathbf{U}|=1$，从而有$|\mathbf{U}|=\mathrm{e}^{\mathrm{i}\theta}$，$|\mathbf{U}^\dagger|=\mathrm{e}^{-\mathrm{i}\theta}$。若$\mathbf{U}$的元素均取正实数，则$|\mathbf{U}^\dagger|=|\mathbf{U}|=1$，从而$|\widetilde{\chi}_1\dots\widetilde{\chi}_N\rangle=|\chi_1\dots\chi_N\rangle$，证毕

练习6：推导电子亲和能的表达式$\widetilde{\mathrm{EA}}(N,r)=E_0(N)-\widetilde{E}(N+1,r)=-\varepsilon_r$

解：我们知道

$$\begin{aligned}\widetilde{E}(N+1,r)&=(\sum_{a\neq r}^{N+1}h_{aa}+h_{rr})+\frac{1}{2}(\sum_{a\neq r}^{N+1}\sum_{b\neq r}^{N+1}\langle ab||ab\rangle+\sum_{a}^{N+1}\langle ar||ar\rangle+\sum_{b}^{N+1}\langle rb||rb\rangle)\\&=(\sum_{a\neq r}^{N+1}h_{aa}+\frac{1}{2}\sum_{a\neq r}^{N+1}\sum_{b\neq r}^{N+1}\langle ab||ab\rangle)+(h_{rr}+\frac{1}{2}\sum_{a}^{N+1}\langle ar||ar\rangle+\frac{1}{2}\sum_{b}^{N+1}\langle rb||rb\rangle)\\&=(\sum_{a\neq r}^{N+1}h_{aa}+\frac{1}{2}\sum_{a\neq r}^{N+1}\sum_{b\neq r}^{N+1}\langle ab||ab\rangle)+(h_{rr}+\sum_{a}^{N+1}\langle ar||ar\rangle)\text{（根据}\langle ar||ar\rangle=\langle ra||ra\rangle\text{）}\end{aligned}$$

而$E_0(N)=\sum\limits_a^N h_{aa}+\frac{1}{2}\sum\limits_a^N\sum\limits_b^N\langle ab||ab\rangle$，$\varepsilon_r=h_{rr}+\sum\limits_a^{N+1}\langle ar||ar\rangle$，因此代入得

$\widetilde{E}(N+1,r)=E_0(N)+\varepsilon_r$，即$\widetilde{\mathrm{EA}}(N,r)=E_0(N)-\widetilde{E}(N+1,r)=-\varepsilon_r$

练习7：写出UHF轨道能量的一般表达式

解：由于UHF的Fock算符和HF方程为

$$\hat{f}^{\sigma}(\boldsymbol{r}_1)=\hat{h}(\boldsymbol{r}_1)+\sum_{\sigma'}\sum_{a}^{N_{\sigma'}}\int d\boldsymbol{r}_2\psi_a^{\sigma',*}(\boldsymbol{r}_2)\boldsymbol{r}_{12}^{-1}(1-\delta_{\sigma\sigma'}\mathcal{P}_{12})\psi_a^{\sigma'}(\boldsymbol{r}_2)$$
$$\hat{f}^{\sigma}(\boldsymbol{r}_1)\psi_i^{\sigma}(\boldsymbol{r}_1)=\varepsilon_i^{\sigma}\psi_i^{\sigma}(\boldsymbol{r}_1)$$

因此UHF轨道能量的表达式为

$$\begin{aligned}\varepsilon_i^{\alpha}&=(\psi_i^{\alpha}|\hat{f}^{\alpha}|\psi_i^{\alpha})=\int d\boldsymbol{r}_1\psi_i^{\alpha,*}(\boldsymbol{r}_1)[\hat{h}(\boldsymbol{r}_1)+\sum_a^{N_\alpha}\int d\boldsymbol{r}_2\psi_a^{\alpha,*}(\boldsymbol{r}_2)\boldsymbol{r}_{12}^{-1}(1-\mathcal{P}_{12})\psi_a^{\alpha}(\boldsymbol{r}_2)+\sum_a^{N_\beta}\int d\boldsymbol{r}_2\psi_a^{\beta,*}(\boldsymbol{r}_2)\boldsymbol{r}_{12}^{-1}\psi_a^{\beta}(\boldsymbol{r}_2)]\psi_i^{\alpha}(\boldsymbol{r}_1)\\&=h_{ii}^{\alpha}+\sum_a^{N_\alpha}(J_{ia}^{\alpha\alpha}-K_{ia}^{\alpha\alpha})+\sum_a^{N_\beta}J_{ia}^{\alpha\beta}\end{aligned}$$

$$\begin{aligned}\varepsilon_i^{\beta}&=(\psi_i^{\beta}|\hat{f}^{\beta}|\psi_i^{\beta})=\int d\boldsymbol{r}_1\psi_i^{\beta,*}(\boldsymbol{r}_1)[\hat{h}(\boldsymbol{r}_1)+\sum_a^{N_\beta}\int d\boldsymbol{r}_2\psi_a^{\beta,*}(\boldsymbol{r}_2)\boldsymbol{r}_{12}^{-1}(1-\mathcal{P}_{12})\psi_a^{\beta}(\boldsymbol{r}_2)+\sum_a^{N_\alpha}\int d\boldsymbol{r}_2\psi_a^{\alpha,*}(\boldsymbol{r}_2)\boldsymbol{r}_{12}^{-1}\psi_a^{\alpha}(\boldsymbol{r}_2)]\psi_i^{\beta}(\boldsymbol{r}_1)\\&=h_{ii}^{\beta}+\sum_a^{N_\beta}(J_{ia}^{\beta\beta}-K_{ia}^{\beta\beta})+\sum_a^{N_\alpha}J_{ia}^{\beta\alpha}\end{aligned}$$

练习8：在Roothaan方程中，记密度矩阵元$P_{\mu\nu}\equiv 2\sum\limits_{a=1}^{\frac{N}{2}}C_{\mu a}C_{\nu a}^*$，重叠矩阵元$S_{\mu\nu}\equiv\int d\boldsymbol{r}_1\phi_\mu^*(\boldsymbol{r}_1)\phi_\nu(\boldsymbol{r}_1)$，证明$\mathbf{PSP}=2\mathbf{P}$，特别的，当基组正交归一时，有$\frac{1}{2}\mathbf{P}$为幂等矩阵

证明：根据空间分子轨道的正交（归一）性$\langle\psi_a|\psi_b\rangle=\delta_{ab}$，结合分子轨道按基组展开，得：

$$\sum_{\mu}^{K} C_{\mu a}^{*}\langle\phi_{\mu}|\cdot\sum_{\nu}^{K} C_{\nu b}|\phi_{\nu}\rangle=\sum_{\mu,\nu}^{K} C_{\mu a}^{*} S_{\mu\nu} C_{\nu b}=\delta_{ab}$$

对矩阵$\mathbf{PSP}$的元素$(\mathbf{PSP})_{\mu\nu}$，我们有：

$$\begin{aligned}(\mathbf{PSP})_{\mu\nu}&=\sum_{\eta,\lambda}^{K} P_{\mu\eta} S_{\eta\lambda} P_{\lambda\nu}=\sum_{\eta,\lambda}^{K}(2\sum_{a=1}^{\frac{N}{2}} C_{\mu a} C_{\eta a}^{*}) S_{\eta\lambda}(2\sum_{b=1}^{\frac{N}{2}} C_{\lambda b} C_{\nu b}^{*})=4\sum_{a,b}^{\frac{N}{2}} C_{\mu a} C_{\nu b}^{*}(\sum_{\eta,\lambda}^{K} C_{\eta a}^{*} S_{\eta\lambda} C_{\lambda b})\\&=2\cdot 2\sum_{a,b}^{\frac{N}{2}} C_{\mu a} C_{\nu b}^{*}\delta_{ab}=2\cdot 2\sum_{a=1}^{\frac{N}{2}} C_{\mu a} C_{\nu a}^{*}=2P_{\mu\nu}\end{aligned}$$

因此$\mathbf{PSP}=2\mathbf{P}$，特别的，当基组正交归一时，$S_{\mu\nu}=\delta_{\mu\nu}$，从而$\mathbf{S}=\mathbf{I}$，故
$\mathbf{PSP}=\mathbf{PIP}=\mathbf{P}^2=2\mathbf{P}$，即$(\frac{1}{2}\mathbf{P})^2=\frac{1}{2}\mathbf{P}$，因此$\frac{1}{2}\mathbf{P}$为幂等矩阵

习题4.1

1.直接从自旋限制HF总能量表达式出发应用变分法推导RHF方程

解：RHF的基态能量表达式为$E_0=2\sum_{a}^{\frac{N}{2}} h_{aa}+\sum_{a}^{\frac{N}{2}}\sum_{b}^{\frac{N}{2}}(2J_{ab}-K_{ab})$，因此定义辅助泛函

$$L=E_0-2\sum_{a}^{\frac{N}{2}}\sum_{b}^{\frac{N}{2}}\lambda_{ba}(\langle\psi_a|\psi_b\rangle-\delta_{ab})\text{（这是因为}\langle\chi_{2i-1}|\chi_{2i-1}\rangle=\langle\chi_{2i}|\chi_{2i}\rangle=1,\langle\chi_{2i-1}|\chi_{2i}\rangle=\langle\chi_{2i-1}|\chi_{2i}\rangle=0\text{）}$$

并假定$\lambda_{ba}=\lambda_{ab}^{*}$，则对辅助泛函两边求变分，并令$\delta L=0$，得：

$$\begin{aligned}\delta L&=\delta E_0-2\sum_{a}^{\frac{N}{2}}\sum_{b}^{\frac{N}{2}}\lambda_{ba}(\langle\delta\psi_a|\psi_b\rangle+\langle\psi_a|\delta\psi_b\rangle)\\&=2\sum_{a}^{\frac{N}{2}}(\langle\delta\psi_a|\hat{h}|\psi_a\rangle+\langle\psi_a|\hat{h}|\delta\psi_a\rangle)+2\sum_{a}^{\frac{N}{2}}\sum_{b}^{\frac{N}{2}}(\langle\delta\psi_a\psi_b|\psi_a\psi_b\rangle+\langle\psi_a\delta\psi_b|\psi_a\psi_b\rangle+\langle\psi_a\psi_b|\delta\psi_a\psi_b\rangle+\langle\psi_a\psi_b|\psi_a\delta\psi_b\rangle)\\&\quad-\sum_{a}^{\frac{N}{2}}\sum_{b}^{\frac{N}{2}}(\langle\delta\psi_a\psi_b|\psi_b\psi_a\rangle+\langle\psi_a\delta\psi_b|\psi_b\psi_a\rangle+\langle\psi_a\psi_b|\delta\psi_b\psi_a\rangle+\langle\psi_a\psi_b|\psi_b\delta\psi_a\rangle)-2\sum_{a}^{\frac{N}{2}}\sum_{b}^{\frac{N}{2}}\lambda_{ba}(\langle\delta\psi_a|\psi_b\rangle+\langle\psi_a|\delta\psi_b\rangle)\\&=2\sum_{a}^{\frac{N}{2}}(\langle\delta\psi_a|\hat{h}|\psi_a\rangle+\langle\psi_a|\hat{h}|\delta\psi_a\rangle)+2\sum_{a}^{\frac{N}{2}}\sum_{b}^{\frac{N}{2}}(2\langle\delta\psi_a\psi_b|\psi_a\psi_b\rangle+2\langle\psi_a\psi_b|\delta\psi_a\psi_b\rangle)-\sum_{a}^{\frac{N}{2}}\sum_{b}^{\frac{N}{2}}(2\langle\delta\psi_a\psi_b|\psi_b\psi_a\rangle+2\langle\psi_a\psi_b|\delta\psi_b\psi_a\rangle)\\&\quad-2\sum_{a}^{\frac{N}{2}}\sum_{b}^{\frac{N}{2}}(\lambda_{ba}\langle\delta\psi_a|\psi_b\rangle+\lambda_{ab}\langle\psi_b|\delta\psi_a\rangle)\quad\text{（交换哑标并不会影响计算结果）}\\&=2\sum_{a}^{\frac{N}{2}}\langle\delta\psi_a|\hat{h}|\psi_a\rangle+4\sum_{a}^{\frac{N}{2}}\sum_{b}^{\frac{N}{2}}\langle\delta\psi_a\psi_b|\psi_a\psi_b\rangle-2\sum_{a}^{\frac{N}{2}}\sum_{b}^{\frac{N}{2}}\langle\delta\psi_a\psi_b|\psi_b\psi_a\rangle-2\sum_{a}^{\frac{N}{2}}\sum_{b}^{\frac{N}{2}}\lambda_{ba}\langle\delta\psi_a|\psi_b\rangle+\text{复共轭部分}=0\end{aligned}$$

因此有

$$[\hat{h}(\boldsymbol{r}_1)+\sum_{b}^{\frac{N}{2}}\int d\boldsymbol{r}_2\psi_b^{*}(\boldsymbol{r}_2)\boldsymbol{r}_{12}^{-1}(2-\mathcal{P}_{12})\psi_b(\boldsymbol{r}_2)]\psi_a(\boldsymbol{r}_1)=\sum_{b}^{\frac{N}{2}}\lambda_{ba}\psi_b(\boldsymbol{r}_1)$$

记$\hat{f}(\boldsymbol{r}_1)=\hat{h}(\boldsymbol{r}_1)+\sum_{b}^{\frac{N}{2}}\int d\boldsymbol{r}_2\psi_b^{*}(\boldsymbol{r}_2)\boldsymbol{r}_{12}^{-1}(2-\mathcal{P}_{12})\psi_b(\boldsymbol{r}_2)]$，则有$\lambda_{ba}=\langle\psi_b|\hat{f}|\psi_a\rangle$，且以$\lambda_{ba}$为矩阵元，可构成厄米矩阵$\mathbf{\Lambda}$，这个矩阵可通过幺正变换$\mathbf{U}$，变为$\mathbf{\Lambda}=\mathbf{U}^{-1}\mathbf{EU}$，其中
$\mathbf{E}=\mathrm{diag}[\varepsilon_1,\varepsilon_2,\ldots,\varepsilon_{\frac{N}{2}}]$，相应的，若将波函数写作行矩阵的形式$\mathbf{\Psi}=[\psi_1,\psi_2,\ldots,\psi_{\frac{N}{2}}]$，则有
$\hat{f}\mathbf{\Psi}=\mathbf{\Psi\Lambda}=\mathbf{\Psi U}^{-1}\mathbf{EU}$，两边右乘，得$\hat{f}\mathbf{\Psi U}^{-1}=\hat{f}(\mathbf{\Psi U}^{-1})=(\mathbf{\Psi U}^{-1})\mathbf{E}$，可以证明Fock算符

在轨道幺正变换下不变（证明略），因此最终我们可以得到正则化的RHF方程：

$$[\hat{h}(\boldsymbol{r}_1)+\sum_b^{\frac{N}{2}}\int d\boldsymbol{r}_2\psi_b^*(\boldsymbol{r}_2)\boldsymbol{r}_{12}^{-1}(2-\mathcal{P}_{12})\psi_b(\boldsymbol{r}_2)]\psi_a(\boldsymbol{r}_1)=\varepsilon_a\psi_a(\boldsymbol{r}_1)$$

2.用UHF方法描述Li原子基态电子构型，请问：（1）$\varepsilon_{1s}^{\alpha}$和$\varepsilon_{1s}^{\beta}$两个轨道能量相等吗？如不等，哪个更低一些？为什么？（2）$\varepsilon_{2s}^{\alpha}$和$\varepsilon_{2s}^{\beta}$和两个轨道能量相等吗？如不等，哪个更低一些？为什么？

解：根据UHF方法，我们知道：

$$\begin{cases}\varepsilon_{1s}^{\alpha}=h_{1s,1s}^{\alpha}+J_{1s,2s}^{\alpha\alpha}-K_{1s,2s}^{\alpha\alpha}+J_{1s,1s}^{\alpha\beta}\\ \varepsilon_{1s}^{\beta}=h_{1s,1s}^{\beta}+J_{1s,1s}^{\beta\alpha}+J_{1s,2s}^{\beta\alpha}\\ \varepsilon_{2s}^{\alpha}=h_{2s,2s}^{\alpha}+J_{2s,1s}^{\alpha\alpha}-K_{2s,1s}^{\alpha\alpha}+J_{2s,1s}^{\alpha\beta}\\ \varepsilon_{2s}^{\beta}=h_{2s,2s}^{\beta}+J_{2s,1s}^{\beta\beta}-K_{2s,1s}^{\beta\beta}+J_{2s,1s}^{\beta\alpha}+J_{2s,2s}^{\beta\alpha}\end{cases}$$

由于Li原子中α电子（自旋向上的电子）比β电子（自旋向下的电子）多1，因此对轨道ψ_{1s}^{α}和ψ_{1s}^{β}，ψ_{1s}^{α}处的电子将受到交换势的影响，导致轨道能量下降，即$\varepsilon_{1s}^{\alpha}<\varepsilon_{1s}^{\beta}$；对轨道$\psi_{2s}^{\alpha}$和$\psi_{2s}^{\beta}$，$\psi_{2s}^{\beta}$将受到库仑势的影响，导致轨道能量上升，即$\varepsilon_{2s}^{\alpha}<\varepsilon_{2s}^{\beta}$