## 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 $\hat{\Gamma}^2 
eq \hat{\Gamma}$ 

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

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

从而有

$$\mathrm{Tr}(\hat{\Gamma}) = \int (oldsymbol{x}^N |\hat{\Gamma}|oldsymbol{x}^N) doldsymbol{x}^N = \int (oldsymbol{x}^N |\sum_i p_i |\Psi_i
angle \langle \Psi_i| \cdot |oldsymbol{x}^N) doldsymbol{x}^N = \int \sum_i p_i (oldsymbol{x}^N |\Psi_i
angle \langle \Psi_i|oldsymbol{x}^N) doldsymbol{x}^N = \sum_i p_i = 1$$

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

此处利用到 $|\Psi_i
angle 
eq |\Psi_j
angle$ ,、 $\langle\Psi_i|\Psi_i
angle = \langle\Psi_j|\Psi_j
angle = 1$ ,因此 ${
m Tr}(\hat{\Gamma}^2) 
eq {
m Tr}(\hat{\Gamma})$ ,从而 $\hat{\Gamma}^2 
eq \hat{\Gamma}$ ,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

$$egin{aligned} \gamma_1(oldsymbol{x}_1^{'};oldsymbol{x}_1) &= N \int \cdots \int \gamma_N(oldsymbol{x}_1^{'},oldsymbol{x}_2^{'},\ldots,oldsymbol{x}_N^{'};oldsymbol{x}_1,oldsymbol{x}_2,\ldots,oldsymbol{x}_N) doldsymbol{x}_2\ldots doldsymbol{x}_N \end{aligned}$$

二阶约化密度矩阵为

$$\gamma_2(m{x}_1^{'},m{x}_2^{'};m{x}_1,m{x}_2) = rac{N(N-1)}{2} \int \cdots \int \gamma_N(m{x}_1^{'},m{x}_2^{'},\ldots,m{x}_N^{'};m{x}_1,m{x}_2,\ldots,m{x}_N) dm{x}_3\ldots dm{x}_N$$

因此代入得

$$egin{aligned} \gamma_1(oldsymbol{x}_1';oldsymbol{x}_1) &= N\int [\int \cdots \int \gamma_N(oldsymbol{x}_1',oldsymbol{x}_2',\dots,oldsymbol{x}_N';oldsymbol{x}_1,oldsymbol{x}_2',\dots,oldsymbol{x}_N';oldsymbol{x}_1,oldsymbol{x}_2,\dots,oldsymbol{x}_N) \dots doldsymbol{x}_N] doldsymbol{x}_2 \ &= N\int rac{2}{N(N-1)} \gamma_2(oldsymbol{x}_1',oldsymbol{x}_2';oldsymbol{x}_1,oldsymbol{x}_1,oldsymbol{x}_1,oldsymbol{x}_2';oldsymbol{x}_2';oldsymbol{x}_1,oldsymbol{x}_2';oldsymbol{x}_1,oldsymbol{x}_2';oldsymbol{x}_2';oldsymbol{x}_1,oldsymbol{x}_2';oldsymbol{x}_2';oldsymbol{x}_1,oldsymbol{x}_2';oldsymbol{x}_2';oldsymbol{x}_2';oldsymbol{x}_1,oldsymbol{x}_2';oldsymbol{x}_2';$$

# 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

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

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

$$h_{ij} = \langle \chi_i(m{x}_1) | \hat{h}(m{x}_1) | \chi_j(m{x}_1) 
angle = \int \chi_i^*(m{x}_1) \hat{h}(m{r}_1) \chi_j(m{x}_1) dm{x}$$
  $\langle \chi_i(m{x}_1) | \hat{J}_k(m{x}_1) | \chi_j(m{x}_1) 
angle \equiv \langle ik | jk 
angle = \int dm{x}_1 \int dm{x}_2 \chi_i^*(m{x}_1) \chi_k^*(m{x}_2) m{r}_{12}^{-1} \chi_j(m{x}_1) \chi_k(m{x}_2)$   $\langle \chi_i(m{x}_1) | \hat{K}_k(m{x}_1) | \chi_j(m{x}_1) 
angle \equiv \langle ik | kj 
angle = \int dm{x}_1 \int dm{x}_2 \chi_i^*(m{x}_1) \chi_k^*(m{x}_2) m{r}_{12}^{-1} \chi_k(m{x}_1) \chi_j(m{x}_2)$  则对于FOCK算符 $\hat{f}(m{x}_1) = \hat{h}(m{x}_1) + \sum_b^N [\hat{J}_b(m{x}_1) - \hat{K}_b(m{x}_1)]$ ,有 
$$f_{ij} = \langle \chi_i(m{x}_1) | \hat{f}(m{x}_1) | \chi_j(m{x}_1) 
angle = h_{ij} + \sum_b (\langle ib | jb 
angle - \langle ib | bj 
angle)$$
  $f_{ij}^* = \langle \chi_i(m{x}_1) | \hat{f}(m{x}_1) | \chi_j(m{x}_1) 
angle^* = h_{ij}^* + \sum_b (\langle ib | jb 
angle^* - \langle ib | bj 
angle^*) = h_{ji} + \sum_b (\langle jb | ib 
angle - \langle bj | ib 
angle)$   $= h_{ji} + \sum_b (\langle jb | ib 
angle - \langle jb | bi 
angle) = f_{ji}$ 

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  $|\Phi\rangle=|\chi_1\ldots\chi_N\rangle$ 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, $|\Phi\rangle=|\widetilde{\chi}_1\ldots\widetilde{\chi}_N\rangle$ 。

证明:将两个Slater行列式展开,得:

$$|\chi_1 \dots \chi_N 
angle = rac{1}{\sqrt{N!}} egin{array}{ccccc} \chi_1(oldsymbol{x}_1) & \chi_2(oldsymbol{x}_1) & \dots & \chi_N(oldsymbol{x}_1) \ \chi_1(oldsymbol{x}_2) & \chi_2(oldsymbol{x}_2) & \dots & \chi_N(oldsymbol{x}_2) \ dots & dots & dots & \ddots & dots \ \chi_1(oldsymbol{x}_N) & \chi_2(oldsymbol{x}_N) & \dots & \chi_N(oldsymbol{x}_N) \end{array}$$

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

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 $|\mathbf{A}\mathbf{B}|=|\mathbf{A}||\mathbf{B}|)$ ,我们有

$$|\widetilde{\chi}_1 \ldots \widetilde{\chi}_N 
angle = |\chi_1 \ldots \chi_N 
angle \cdot |\mathbf{U}^\dagger|$$
,其中 $|\mathbf{U}^\dagger| = egin{bmatrix} U_{11}^* & U_{21}^* & \ldots & U_{N1}^* \ U_{12}^* & U_{22}^* & \ldots & U_{N2}^* \ dots & dots & \ddots & dots \ U_{1N}^* & U_{2N}^* & \ldots & U_{NN}^* \ \end{pmatrix}$ ,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 $|\widetilde{\chi}_1\ldots\widetilde{\chi}_N\rangle=|\chi_1\ldots\chi_N\rangle$ ,证毕

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

解: 我们知道

$$egin{aligned} \widetilde{E}(N+1,r) &= (\sum_{a
eq r}^{N+1}h_{aa} + h_{rr}) + rac{1}{2}(\sum_{a
eq r}^{N+1}\sum_{b
eq r}^{N+1}\langle ab||ab
angle + \sum_{a}^{N+1}\langle ar||ar
angle + \sum_{b}^{N+1}\langle rb||rb
angle) \\ &= (\sum_{a
eq r}^{N+1}h_{aa} + rac{1}{2}\sum_{a
eq r}^{N+1}\sum_{b
eq r}^{N+1}\langle ab||ab
angle) + (h_{rr} + rac{1}{2}\sum_{a}^{N+1}\langle ar||ar
angle + rac{1}{2}\sum_{b}^{N+1}\langle rb||rb
angle) \\ &= (\sum_{a
eq r}^{N+1}h_{aa} + rac{1}{2}\sum_{a
eq r}^{N+1}\sum_{b
eq r}^{N+1}\langle ab||ab
angle) + (h_{rr} + \sum_{a}^{N+1}\langle ar||ar
angle) &\in \mathbb{R} \ \langle ar||ar
angle = \langle ra||ra
angle) \end{aligned}$$

而
$$E_0(N)=\sum\limits_a^Nh_{aa}+rac{1}{2}\sum\limits_a^N\sum\limits_b^N\langle ab||ab
angle$$
, $arepsilon_r=h_{rr}+\sum\limits_a^{N+1}\langle ar||ar
angle$ ,因此代入得 $\widetilde{E}(N+1,r)=E_0(N)+arepsilon_r$ ,即 $\widetilde{\mathrm{EA}}(N,r)=E_0(N)-\widetilde{E}(N+1,r)=-arepsilon_r$ 

#### 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

$$egin{aligned} \hat{f}^{\sigma}(oldsymbol{r}_1) &= \hat{h}(oldsymbol{r}_1) + \sum_{\sigma^{'}} \sum_{a}^{N_{\sigma^{'}}} \int doldsymbol{r}_2 \psi^{\sigma^{'},*}_a(oldsymbol{r}_2) oldsymbol{r}_{12}^{-1} (1 - \delta_{\sigma\sigma^{'}} \mathcal{P}_{_{12}}) \psi^{\sigma^{'}}_a(oldsymbol{r}_2) \ \hat{f}^{\sigma}(oldsymbol{r}_1) \psi^{\sigma}_i(oldsymbol{r}_1) &= arepsilon_i^{\sigma} \psi^{\sigma}_i(oldsymbol{r}_1) \end{aligned}$$

因此UHF轨道能量的表达式为

$$egin{aligned} arepsilon_i^lpha &= (\psi_i^lpha|\hat{f}^lpha|\psi_i^lpha) = \int dm{r}_1 \psi_i^{lpha,*}(m{r}_1)[\hat{h}(m{r}_1) + \sum_a^{N_lpha} \int dm{r}_2 \psi_a^{lpha,*}(m{r}_2)m{r}_{12}^{-1}(1-\mathcal{P}_{12})\psi_a^lpha(m{r}_2) + \sum_a^{N_eta} \int dm{r}_2 \psi_a^{eta,*}(m{r}_2)m{r}_{12}^{-1}\psi_a^eta(m{r}_2)]\psi_i^lpha(m{r}_1) &= h_{ii}^lpha + \sum_a^{N_lpha} (J_{ia}^{lphalpha} - K_{ia}^{lphalpha}) + \sum_a^{N_eta} J_{ia}^{lphaeta} &= h_{ii}^lpha + \sum_a^{N_lpha} (J_{ia}^{lphalpha} - K_{ia}^{lphalpha}) + \sum_a^{N_eta} J_{ia}^{lphaeta} &= h_{ii}^lpha + \sum_a^{N_lpha} (J_{ia}^{lphalpha} - K_{ia}^{lphalpha}) + \sum_a^{N_eta} J_{ia}^{lphaeta} &= h_{ii}^lpha + \sum_a^{N_lpha} (J_{ia}^{lphalpha} - K_{ia}^{lphalpha}) + \sum_a^{N_eta} J_{ia}^{lphaeta} &= h_{ii}^lpha + \sum_a^{N_lpha} (J_{ia}^{lphalpha} - K_{ia}^{lphalpha}) + \sum_a^{N_lpha} J_{ia}^{lphaeta} &= h_{ii}^lpha + \sum_a^{N_lpha} (J_{ia}^{lphalpha} - K_{ia}^{lphalpha}) + \sum_a^{N_lpha} J_{ia}^{lphaeta} &= h_{ii}^lpha + \sum_a^{N_lpha} (J_{ia}^{lphalpha} - K_{ia}^{lphalpha}) + \sum_a^{N_lpha} J_{ia}^{lphaeta} &= h_{ii}^lpha + \sum_a^{N_lpha} (J_{ia}^{lphalpha} - K_{ia}^lpha) + \sum_a^{N_lpha} J_{ia}^{lphaeta} &= h_{ii}^lpha + \sum_a^{N_lpha} (J_{ia}^lpha - K_{ia}^lpha) + \sum_a^{N_lpha} J_{ia}^lpha + \sum_a^{$$

$$\begin{split} \varepsilon_{i}^{\beta} &= (\psi_{i}^{\beta} | \hat{f}^{\beta} | \psi_{i}^{\beta}) = \int d\boldsymbol{r}_{1} \psi_{i}^{\beta,*}(\boldsymbol{r}_{1}) [\hat{h}(\boldsymbol{r}_{1}) + \sum_{a}^{N_{\beta}} \int d\boldsymbol{r}_{2} \psi_{a}^{\beta,*}(\boldsymbol{r}_{2}) \boldsymbol{r}_{12}^{-1} (1 - \mathcal{P}_{12}) \psi_{a}^{\beta}(\boldsymbol{r}_{2}) + \sum_{a}^{N_{\alpha}} \int d\boldsymbol{r}_{2} \psi_{a}^{\alpha,*}(\boldsymbol{r}_{2}) \boldsymbol{r}_{12}^{-1} \psi_{a}^{\alpha}(\boldsymbol{r}_{2})] \psi_{i}^{\beta}(\boldsymbol{r}_{1}) \\ &= h_{ii}^{\beta} + \sum_{a}^{N_{\beta}} (J_{ia}^{\beta\beta} - K_{ia}^{\beta\beta}) + \sum_{a}^{N_{\alpha}} J_{ia}^{\beta\alpha} \end{split}$$

练习8:在Roothaan方程中,记密度矩阵元 $P_{\mu\nu}\equiv 2\sum_{a=1}^{rac{N}{2}}C_{\mu a}C_{
u a}^*$ ,重叠矩阵元 $S_{\mu
u}\equiv \int dm{r}_1\phi_\mu^*(m{r}_1)\phi_
u(m{r}_1)$ ,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 $\langle \psi_a | \psi_b 
angle = \delta_{ab}$ ,结合分子轨道按基组展开,得:

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

对矩阵PSP的元素 $(PSP)_{\mu\nu}$ , 我们有:

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

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 $E_0=2\sum\limits_a^{rac{N}{2}}h_{aa}+\sum\limits_a^{rac{N}{2}}\sum\limits_b^{rac{N}{2}}(2J_{ab}-K_{ab})$ ,因此定义辅助泛函

$$L=E_0-2\sum_a^{rac{N}{2}}\sum_b^{rac{N}{2}}\lambda_{ba}(\langle\psi_a|\psi_b
angle-\delta_{ab})$$
(这是因为 $\langle\chi_{2i-1}|\chi_{2i-1}
angle=\langle\chi_{2i}|\chi_{2i}
angle=1,\langle\chi_{2i-1}|\chi_{2i}
angle=\langle\chi_{2i-1}|\chi_{2i}
angle=0$ )

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

因此有

$$[\hat{h}(m{r}_1) + \sum_b^{rac{N}{2}} \int dm{r}_2 \psi_b^*(m{r}_2) m{r}_{12}^{-1} (2 - \mathcal{P}_{12}) \psi_b(m{r}_2)] \psi_a(m{r}_1) = \sum_b^{rac{N}{2}} \lambda_{ba} \psi_b(m{r}_1)$$

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 $\Lambda$ ,这个矩阵可通过幺正变换 $\mathbf{U}$ ,变为 $\Lambda = \mathbf{U}^{-1}\mathbf{E}\mathbf{U}$ ,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  $\hat{f}\mathbf{\Psi} = \mathbf{\Psi}\mathbf{\Lambda} = \mathbf{\Psi}\mathbf{U}^{-1}\mathbf{E}\mathbf{U}$ ,两边右乘,得 $\hat{f}\mathbf{\Psi}\mathbf{U}^{-1} = \hat{f}(\mathbf{\Psi}\mathbf{U}^{-1}) = (\mathbf{\Psi}\mathbf{U}^{-1})\mathbf{E}$ ,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:

$$[\hat{h}(m{r}_1) + \sum_{b}^{rac{N}{2}} \int dm{r}_2 \psi_b^*(m{r}_2) m{r}_{12}^{-1} (2 - \mathcal{P}_{12}) \psi_b(m{r}_2)] \psi_a(m{r}_1) = arepsilon_a \psi_a(m{r}_1)$$

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 $\alpha$ 电子(自旋向上的电子)比 $\beta$ 电子(自旋向下的电子)多1,因此对轨道 $\psi_{1s}^{\alpha}$ 和 $\psi_{1s}^{\beta}$ , $\psi_{1s}^{\alpha}$ 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 $\varepsilon_{2s}^{\alpha}<\varepsilon_{2s}^{\beta}$