课堂练习

练习1:写出施密特正交化过程对应的X矩阵

解:基组变换的表达式为

$$ig(\ket{\phi_1'} \quad \ket{\phi_2'} \quad \dots \quad \ket{\phi_n'}ig) = ig(\ket{\phi_1} \quad \ket{\phi_2} \quad \dots \quad \ket{\phi_n}ig)oldsymbol{X}$$

以
$$n=2$$
为例,首先将 $|\phi_1\rangle$ 归一化,得 $|\phi_1'\rangle=rac{|\phi_1
angle}{\langle\phi_1|\phi_1
angle^{rac{1}{2}}}$,其中归一化系数为 $lpha_1=rac{1}{\langle\phi_1|\phi_1
angle^{rac{1}{2}}}$,然后设 $|\phi_2'
angle\rangle=lpha_2(|\phi_2
angle-|\phi_1'
angle\langle\phi_1'|\phi_2
angle)$,则

$$\langle \phi_2^{'} | \phi_2^{'} \rangle = |\alpha_2|^2 (\langle \phi_2 | \phi_2 \rangle - \langle \phi_2 | \phi_1^{'} \rangle \langle \phi_1^{'} | \phi_2 \rangle - \langle \phi_1^{'} | \phi_2 \rangle \langle \phi_2 | \phi_1^{'} \rangle + \langle \phi_2 | \phi_1^{'} \rangle \langle \phi_1^{'} | \phi_1^{'} \rangle \langle \phi_1^{'} | \phi_2 \rangle) = |\alpha_2|^2 (\langle \phi_2 | \phi_2 \rangle - \langle \phi_2 | \phi_1^{'} \rangle \langle \phi_1^{'} | \phi_2 \rangle) = 1$$

解得
$$lpha_2=(rac{\langle\phi_1|\phi_1
angle}{\langle\phi_1|\phi_1
angle\langle\phi_2|\phi_1
angle})^{rac{1}{2}}$$
(取实数解),因此

$$|\phi_2^{'}\rangle = \alpha_2(|\phi_2\rangle - |\phi_1^{'}\rangle\langle\phi_1^{'}|\phi_2\rangle) = (\frac{\langle\phi_1|\phi_1\rangle}{\langle\phi_1|\phi_1\rangle\langle\phi_2|\phi_2\rangle - \langle\phi_1|\phi_2\rangle\langle\phi_2|\phi_1\rangle})^{\frac{1}{2}}|\phi_2\rangle - \frac{\langle\phi_1|\phi_2\rangle}{[\langle\phi_1|\phi_1\rangle(\langle\phi_1|\phi_1\rangle\langle\phi_2|\phi_2\rangle - \langle\phi_1|\phi_2\rangle\langle\phi_2|\phi_1\rangle)]^{\frac{1}{2}}}|\phi_1\rangle$$

$$\begin{split} |\phi_2^{'}\rangle\langle\phi_2^{'}| &= \frac{\langle\phi_1|\phi_1\rangle}{\langle\phi_1|\phi_1\rangle\langle\phi_2|\phi_2\rangle - \langle\phi_1|\phi_2\rangle\langle\phi_2|\phi_1\rangle} |\phi_2\rangle\langle\phi_2| - \frac{\langle\phi_2|\phi_1\rangle}{\langle\phi_1|\phi_1\rangle\langle\phi_2|\phi_2\rangle - \langle\phi_1|\phi_2\rangle\langle\phi_2|\phi_1\rangle} |\phi_2\rangle\langle\phi_1| \\ &- \frac{\langle\phi_1|\phi_2\rangle}{\langle\phi_1|\phi_1\rangle\langle\phi_2|\phi_2\rangle - \langle\phi_1|\phi_2\rangle\langle\phi_2|\phi_1\rangle} |\phi_1\rangle\langle\phi_2| + \frac{\langle\phi_1|\phi_1\rangle\langle\phi_2|\phi_2\rangle - \langle\phi_1|\phi_2\rangle\langle\phi_2|\phi_1\rangle}{\langle\phi_1|\phi_1\rangle\langle\langle\phi_2|\phi_2\rangle - \langle\phi_1|\phi_2\rangle\langle\phi_2|\phi_1\rangle} |\phi_1\rangle\langle\phi_1| \end{split}$$

接下来考虑n=3的情形,设 $|\phi_3'\rangle=lpha_3(|\phi_3\rangle-|\phi_2'\rangle\langle\phi_2'|\phi_3\rangle-|\phi_1'\rangle\langle\phi_1'|\phi_3\rangle)$,则

$$\begin{split} \langle \phi_3' | \phi_3' \rangle &= |\alpha_3|^2 (\langle \phi_3 | \phi_3 \rangle - \langle \phi_3 | \phi_2' \rangle \langle \phi_2' | \phi_3 \rangle - \langle \phi_3 | \phi_1' \rangle \langle \phi_1' | \phi_3 \rangle \\ &- \langle \phi_2' | \phi_3 \rangle \langle \phi_3 | \phi_2' \rangle + \langle \phi_3 | \phi_2' \rangle \langle \phi_2' | \phi_3 \rangle + \langle \phi_3 | \phi_2' \rangle \langle \phi_2' | \phi_3 \rangle \\ &- \langle \phi_1' | \phi_3 \rangle \langle \phi_3 | \phi_1' \rangle + \langle \phi_3 | \phi_1' \rangle \langle \phi_1' | \phi_2 \rangle \langle \phi_2' | \phi_3 \rangle + \langle \phi_3 | \phi_1' \rangle \langle \phi_1' | \phi_3 \rangle \\ &= |\alpha_3|^2 (\langle \phi_3 | \phi_3 \rangle - \langle \phi_3 | \phi_2' \rangle \langle \phi_2' | \phi_3 \rangle - \langle \phi_3 | \phi_1' \rangle \langle \phi_1' | \phi_3 \rangle) \\ &= |\alpha_3|^2 (\langle \phi_3 | \phi_3 \rangle - \frac{\langle \phi_1 | \phi_1 \rangle \langle \phi_3 | \phi_2 \rangle \langle \phi_2 | \phi_3 \rangle - \langle \phi_2 | \phi_1 \rangle \langle \phi_3 | \phi_2 \rangle \langle \phi_1 | \phi_3 \rangle - \langle \phi_1 | \phi_2 \rangle \langle \phi_3 | \phi_1 \rangle \langle \phi_2 | \phi_3 \rangle }{\langle \phi_1 | \phi_1 \rangle \langle \phi_2 | \phi_2 \rangle - \langle \phi_1 | \phi_2 \rangle \langle \phi_2 | \phi_1 \rangle } \\ &- \frac{\langle \phi_1 | \phi_2 \rangle \langle \phi_2 | \phi_1 \rangle \langle \phi_3 | \phi_1 \rangle \langle \phi_1 | \phi_3 \rangle }{\langle \phi_1 | \phi_1 \rangle \langle (\phi_1 | \phi_1 \rangle \langle \phi_2 | \phi_2 \rangle - \langle \phi_1 | \phi_2 \rangle \langle \phi_2 | \phi_1 \rangle)} - \frac{\langle \phi_3 | \phi_1 \rangle \langle \phi_1 | \phi_3 \rangle }{\langle \phi_1 | \phi_1 \rangle } \\ &- \frac{\langle \phi_1 | \phi_2 \rangle \langle \phi_2 | \phi_1 \rangle \langle \phi_3 | \phi_1 \rangle \langle \phi_1 | \phi_3 \rangle }{\langle \phi_1 | \phi_1 \rangle \langle (\phi_1 | \phi_1 \rangle \langle \phi_2 | \phi_2 \rangle - \langle \phi_1 | \phi_2 \rangle \langle \phi_2 | \phi_1 \rangle)} - \frac{\langle \phi_3 | \phi_1 \rangle \langle \phi_1 | \phi_3 \rangle }{\langle \phi_1 | \phi_1 \rangle \langle \phi_2 | \phi_3 \rangle - \langle \phi_1 | \phi_2 \rangle \langle \phi_2 | \phi_1 \rangle)} \\ &- \frac{\langle \phi_3 | \phi_1 \rangle (\langle \phi_1 | \phi_1 \rangle \langle \phi_2 | \phi_2 \rangle - \langle \phi_1 | \phi_2 \rangle \langle \phi_2 | \phi_1 \rangle)}{\langle \phi_1 | \phi_1 \rangle \langle \phi_2 | \phi_2 \rangle - \langle \phi_1 | \phi_2 \rangle \langle \phi_2 | \phi_1 \rangle)} - \frac{\langle \phi_3 | \phi_2 \rangle (\langle \phi_1 | \phi_1 \rangle \langle \phi_2 | \phi_3 \rangle - \langle \phi_1 | \phi_3 \rangle \langle \phi_2 | \phi_1 \rangle)}{\langle \phi_1 | \phi_1 \rangle \langle \phi_2 | \phi_2 \rangle - \langle \phi_1 | \phi_2 \rangle \langle \phi_2 | \phi_1 \rangle)} \\ &+ \frac{\langle \phi_3 | \phi_1 \rangle (\langle \phi_1 | \phi_2 \rangle \langle \phi_2 | \phi_3 \rangle - \langle \phi_1 | \phi_3 \rangle \langle \phi_2 | \phi_2 \rangle)}{\langle \phi_1 | \phi_1 \rangle \langle \phi_2 | \phi_2 \rangle - \langle \phi_1 | \phi_2 \rangle \langle \phi_2 | \phi_1 \rangle}} \\ &- | \alpha_3 |^2 \begin{vmatrix} \langle \phi_1 | \phi_1 \rangle \langle \phi_2 | \phi_2 \rangle - \langle \phi_1 | \phi_3 \rangle \langle \phi_2 | \phi_2 \rangle)}{\langle \phi_1 | \phi_1 \rangle \langle \phi_2 | \phi_2 \rangle - \langle \phi_1 | \phi_3 \rangle \langle \phi_2 | \phi_2 \rangle }} \end{vmatrix} \\ &= | \alpha_3 |^2 \begin{vmatrix} \langle \phi_1 | \phi_1 \rangle \langle \phi_2 | \phi_2 \rangle - \langle \phi_1 | \phi_3 \rangle \langle \phi_2 | \phi_3 \rangle \\ &- \langle \phi_1 | \phi_1 \rangle \langle \phi_2 | \phi_2 \rangle - \langle \phi_1 | \phi_2 \rangle \langle \phi_2 | \phi_1 \rangle)} \end{vmatrix} \\ &= | \alpha_3 |^2 \begin{vmatrix} \langle \phi_1 | \phi_1 \rangle \langle \phi_2 | \phi_2 \rangle - \langle \phi_1 | \phi_3 \rangle \langle \phi_2 | \phi_1 \rangle \\ &- \langle \phi_1 | \phi_1 \rangle \langle \phi_2 | \phi_2 \rangle - \langle \phi_1 | \phi_2 \rangle \langle \phi_2 | \phi_1 \rangle \\ &- \langle \phi_1 | \phi_1 \rangle \langle \phi_2 | \phi_2 \rangle - \langle \phi_1 | \phi_2 \rangle \langle \phi_2 | \phi_1 \rangle)} \end{vmatrix} \\ &= | \alpha_3 |^2 \begin{vmatrix} \langle \phi_1 | \phi_1 \rangle \langle \phi_1 | \phi_1 \rangle \langle \phi_1 | \phi_1 \rangle \langle$$

解得
$$lpha_3 = \left(\begin{vmatrix} \langle \phi_1 | \phi_1 \rangle & \langle \phi_1 | \phi_2 \rangle \\ \langle \phi_2 | \phi_1 \rangle & \langle \phi_2 | \phi_2 \rangle \end{vmatrix} \begin{vmatrix} \langle \phi_1 | \phi_1 \rangle & \langle \phi_1 | \phi_2 \rangle & \langle \phi_1 | \phi_3 \rangle \\ \langle \phi_2 | \phi_1 \rangle & \langle \phi_2 | \phi_2 \rangle & \langle \phi_2 | \phi_3 \rangle \\ \langle \phi_3 | \phi_1 \rangle & \langle \phi_3 | \phi_2 \rangle & \langle \phi_3 | \phi_3 \rangle \end{vmatrix}^{-1}$$
(取实数解), 因此

$$\begin{split} |\phi_3'\rangle &= \alpha_3(|\phi_3\rangle - |\phi_2'\rangle\langle\phi_2'|\phi_3\rangle - |\phi_1'\rangle\langle\phi_1'|\phi_3\rangle) \\ &= (\begin{vmatrix} \langle\phi_1|\phi_1\rangle & \langle\phi_1|\phi_2\rangle \\ \langle\phi_2|\phi_1\rangle & \langle\phi_2|\phi_2\rangle \end{vmatrix} \begin{vmatrix} \langle\phi_1|\phi_1\rangle & \langle\phi_1|\phi_2\rangle & \langle\phi_1|\phi_3\rangle \\ \langle\phi_2|\phi_1\rangle & \langle\phi_2|\phi_2\rangle & \langle\phi_2|\phi_3\rangle \end{vmatrix}^{-1})^{\frac{1}{2}} (|\phi_3\rangle - \frac{\langle\phi_1|\phi_1\rangle\langle\phi_2|\phi_3\rangle}{|\langle\phi_1|\phi_1\rangle & \langle\phi_1|\phi_2\rangle} |\phi_2\rangle \\ &+ \frac{\langle\phi_2|\phi_1\rangle\langle\phi_1|\phi_3\rangle}{|\langle\phi_1|\phi_1\rangle & \langle\phi_1|\phi_2\rangle} |\phi_2\rangle + \frac{\langle\phi_1|\phi_2\rangle\langle\phi_2|\phi_3\rangle}{|\langle\phi_1|\phi_1\rangle & \langle\phi_1|\phi_2\rangle} |\phi_1\rangle - \frac{\langle\phi_1|\phi_2\rangle\langle\phi_2|\phi_1\rangle\langle\phi_1|\phi_3\rangle}{|\langle\phi_1|\phi_1\rangle & \langle\phi_1|\phi_2\rangle} |\phi_1\rangle - \frac{\langle\phi_1|\phi_2\rangle\langle\phi_2|\phi_1\rangle\langle\phi_1|\phi_3\rangle}{|\langle\phi_1|\phi_1\rangle & \langle\phi_1|\phi_2\rangle & \langle\phi_1|\phi_3\rangle} |\phi_1\rangle - \frac{\langle\phi_1|\phi_2\rangle\langle\phi_2|\phi_1\rangle\langle\phi_1|\phi_3\rangle}{|\langle\phi_2|\phi_1\rangle & \langle\phi_2|\phi_2\rangle} |\phi_1\rangle - \frac{\langle\phi_1|\phi_2\rangle\langle\phi_2|\phi_1\rangle\langle\phi_1|\phi_3\rangle}{|\langle\phi_1|\phi_1\rangle & \langle\phi_1|\phi_2\rangle & \langle\phi_1|\phi_3\rangle} |\phi_1\rangle - \frac{\langle\phi_1|\phi_1\rangle\langle\phi_1|\phi_1\rangle\langle\phi_1|\phi_3\rangle}{|\langle\phi_2|\phi_1\rangle & \langle\phi_2|\phi_2\rangle} |\phi_1\rangle - \frac{\langle\phi_1|\phi_2\rangle\langle\phi_1|\phi_3\rangle}{|\langle\phi_1|\phi_1\rangle & \langle\phi_1|\phi_2\rangle} |\phi_1\rangle - \frac{\langle\phi_1|\phi_1\rangle\langle\phi_1|\phi_1\rangle\langle\phi_1|\phi_2\rangle}{|\langle\phi_2|\phi_1\rangle & \langle\phi_2|\phi_2\rangle} |\phi_1\rangle - \frac{\langle\phi_1|\phi_1\rangle\langle\phi_1|\phi_1\rangle\langle\phi_1|\phi_2\rangle\langle\phi_1|\phi_3\rangle}{|\langle\phi_1|\phi_1\rangle & \langle\phi_1|\phi_2\rangle\langle\phi_1|\phi_3\rangle} |\phi_1\rangle - \frac{\langle\phi_1|\phi_1\rangle\langle\phi_1|\phi_1\rangle\langle\phi_1|\phi_2\rangle\langle\phi_1|\phi_3\rangle}{|\langle\phi_1|\phi_1\rangle & \langle\phi_2|\phi_2\rangle\langle\phi_2|\phi_3\rangle} |\phi_1\rangle - \frac{\langle\phi_1|\phi_1\rangle\langle\phi_1|\phi_2\rangle\langle\phi_1|\phi_3\rangle}{|\langle\phi_2|\phi_1\rangle & \langle\phi_2|\phi_2\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle} |\phi_1\rangle - \frac{\langle\phi_1|\phi_1\rangle\langle\phi_1|\phi_1\rangle\langle\phi_1|\phi_2\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle}{|\langle\phi_1|\phi_1\rangle & \langle\phi_2|\phi_2\rangle\langle\phi_2|\phi_3\rangle\langle\phi_1|\phi_3\rangle} |\phi_1\rangle - \frac{\langle\phi_1|\phi_1\rangle\langle\phi_1|\phi_2\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3\rangle\langle\phi_1|\phi_3$$

一般的,记
$$m{S}_j = egin{pmatrix} \langle \phi_1 | \phi_1 \rangle & \langle \phi_1 | \phi_2 \rangle & \dots & \langle \phi_1 | \phi_j \rangle \\ \langle \phi_2 | \phi_1 \rangle & \langle \phi_2 | \phi_2 \rangle & \dots & \langle \phi_2 | \phi_j \rangle \\ \vdots & \vdots & \ddots & \vdots \\ \langle \phi_3 | \phi_1 \rangle & \langle \phi_3 | \phi_2 \rangle & \dots & \langle \phi_3 | \phi_j \rangle \end{pmatrix}$$
,对应的行列式为 $D_j = \det m{S}_j$,边界条件为 $m{S}_0 = m{I}$, $D_i = 1$,则

$$|\phi_j'
angle = rac{1}{\sqrt{D_{j-1}D_j}}\sum_{i=1}^j |\phi_i
angle ext{cof}_{ji}(oldsymbol{S}_j)$$

其中 $cof_{ii}(S_i)$ 为 S_i 按j行i列展开的代数余子式,于是X矩阵的矩阵元为

$$X_{ij} = egin{cases} rac{1}{\sqrt{D_{j-1}D_{j}}} \mathrm{cof}_{ji}(oldsymbol{S}_{j}) & (i \leq j) \ 0 & (i > j) \end{cases}$$

练习2: 证明按 $\phi'_\mu=\sum\limits_{
u=1}^K\widetilde{X}_{
u\mu}\phi_
u\;(\mu=1,2,\ldots,K^{'})$ 构建的基函数正交归一,其中 $\widetilde{X}_{
u\mu}=U_{
u,\mu}s_\mu^{-rac{1}{2}}$

证明: 对于任意 λ, μ , 我们有:

$$\langle \phi_\lambda^{'} | \phi_\mu^{'} \rangle = \sum_{\eta=1}^K \widetilde{\boldsymbol{X}}_{\eta\lambda}^* \phi_\eta^\dagger \sum_{\nu=1}^K \widetilde{\boldsymbol{X}}_{\nu\mu} \phi_\nu = \sum_{\eta=1}^K \sum_{\nu=1}^K \widetilde{\boldsymbol{X}}_{\eta\lambda}^* \widetilde{\boldsymbol{X}}_{\nu\mu} \langle \phi_\eta | \phi_\nu \rangle = \sum_{\eta=1}^K \sum_{\nu=1}^K U_{\eta,\lambda}^* (s_\lambda^*)^{-\frac{1}{2}} U_{\nu,\mu} s_\mu^{-\frac{1}{2}} S_{\eta\nu}$$

接下来我们要利用 $oldsymbol{U}^\dagger oldsymbol{S} oldsymbol{U} = oldsymbol{s}$ 的性质,左乘 $oldsymbol{U} oldsymbol{S} oldsymbol{U} = oldsymbol{U} oldsymbol{s}$,即

$$(m{S}m{U})_{ab} = \sum\limits_{i=1}^K S_{ai} U_{ib} = \sum\limits_{i=1}^K U_{ai} s_{ib} = (m{U}m{s})_{ab}$$
,且由于 $m{s} = ext{diag}(s_1, s_2, \dots, s_K)$,因此 $s_{ij} = s_{ij} \delta_{ij} = s_i \delta_{ij}$,从而:

$$egin{aligned} \langle \phi_\lambda' | \phi_\mu'
angle &= \sum_{\eta=1}^K \sum_{
u=1}^K U_{\eta,\lambda}^* (s_\lambda^*)^{-rac{1}{2}} s_\mu^{-rac{1}{2}} S_{\eta
u} U_{
u,\mu} = \sum_{\eta=1}^K \sum_{
u=1}^K U_{\eta,\lambda}^* (s_\lambda^*)^{-rac{1}{2}} s_\mu^{-rac{1}{2}} U_{\eta
u} s_{
u\mu} \delta_{
u\mu} \delta_{$$

当 $\lambda \neq \mu$ 时,显然 $\langle \phi_{\lambda}^{'} | \phi_{\mu}^{'} \rangle = 0$;当 $\lambda = \mu$ 时,有 $\langle \phi_{\lambda}^{'} | \phi_{\mu}^{'} \rangle = (s_{\mu}^{*})^{-\frac{1}{2}} s_{\mu}^{\frac{1}{2}}$,而 s_{μ} 为正实数,因此 $\langle \phi_{\lambda}^{'} | \phi_{\mu}^{'} \rangle = 1$,原题得证。

练习3:证明两个1s型的Gauss函数乘积可以转化为另一个1s型的Gauss函数乘积,且满足

$$\phi_{1\mathrm{s}}(m{r}-m{R}_A;lpha_A)\phi_{1\mathrm{s}}(m{r}-m{R}_B;lpha_B) = K_{AB}\phi_{1\mathrm{s}}(m{r}-m{R}_P;lpha_P) \ lpha_P = lpha_A + lpha_B \quad K_{AB} = [rac{2lpha_Alpha_B}{(lpha_A+lpha_B)\pi}]^rac{3}{4}\,\mathrm{e}^{-rac{lpha_Alpha_B}{lpha_A+lpha_B}|m{R}_A-m{R}_B|^2} \quad m{R}_P = rac{lpha_Am{R}_A + lpha_Bm{R}_B}{lpha_A+lpha_B}$$

证明: 1s型Gauss函数的形式为 $\phi_{1
m s}(r,lpha)=(rac{8lpha^3}{\pi^3})^{rac{1}{4}}{
m e}^{-lpha r^2}$,故代入得

$$\begin{split} &\phi_{1\mathrm{s}}(\boldsymbol{r}-\boldsymbol{R}_{A};\alpha_{A})\phi_{1\mathrm{s}}(\boldsymbol{r}-\boldsymbol{R}_{B};\alpha_{B})\\ &=(\frac{8\alpha_{A}^{3}}{\pi^{3}})^{\frac{1}{4}}\mathrm{e}^{-\alpha_{A}|\boldsymbol{r}-\boldsymbol{R}_{A}|^{2}}\cdot(\frac{8\alpha_{B}^{3}}{\pi^{3}})^{\frac{1}{4}}\mathrm{e}^{-\alpha_{B}|\boldsymbol{r}-\boldsymbol{R}_{B}|^{2}}=(\frac{64\alpha_{A}^{3}\alpha_{B}^{3}}{\pi^{6}})^{\frac{1}{4}}\mathrm{e}^{-\alpha_{A}|\boldsymbol{r}-\boldsymbol{R}_{A}|^{2}-\alpha_{B}|\boldsymbol{r}-\boldsymbol{R}_{B}|^{2}}\\ &=(\frac{8\alpha_{P}^{3}}{\pi^{3}})^{\frac{1}{4}}(\frac{2\alpha_{A}\alpha_{B}}{\pi\alpha_{P}})^{\frac{3}{4}}\mathrm{e}^{-\frac{\alpha_{A}\alpha_{B}}{\alpha_{A}+\alpha_{B}}|\boldsymbol{R}_{A}-\boldsymbol{R}_{B}|^{2}}\cdot\mathrm{e}^{-\alpha_{A}|\boldsymbol{r}-\boldsymbol{R}_{A}|^{2}-\alpha_{B}|\boldsymbol{r}-\boldsymbol{R}_{B}|^{2}+\frac{\alpha_{A}\alpha_{B}}{\alpha_{A}+\alpha_{B}}|\boldsymbol{R}_{A}-\boldsymbol{R}_{B}|^{2}}\\ &=K_{AB}(\frac{8\alpha_{P}^{3}}{\pi^{3}})^{\frac{1}{4}}\mathrm{e}^{-\alpha_{A}|\boldsymbol{r}-\boldsymbol{R}_{A}|^{2}-\alpha_{B}|\boldsymbol{r}-\boldsymbol{R}_{B}|^{2}+\frac{\alpha_{A}\alpha_{B}}{\alpha_{A}+\alpha_{B}}|\boldsymbol{R}_{A}-\boldsymbol{R}_{B}|^{2}}\end{split}$$

其中
$$lpha_P=lpha_A+lpha_B$$
, $K_{AB}=(rac{2lpha_Alpha_B}{\pilpha_P})^{rac{3}{4}}{
m e}^{-rac{lpha_Alpha_B}{lpha_A+lpha_B}|{m R}_A-{m R}_B|^2}$,现在我们要证明

$$-lpha_A |oldsymbol{r}-oldsymbol{R}_A|^2 - lpha_B |oldsymbol{r}-oldsymbol{R}_B|^2 + rac{lpha_A lpha_B}{lpha_A + lpha_B} |oldsymbol{R}_A - oldsymbol{R}_B|^2 = -(lpha_A + lpha_B) |oldsymbol{r}-oldsymbol{R}_P|^2$$

其中
$$m{R}_P=rac{lpha_Am{R}_A+lpha_Bm{R}_B}{lpha_A+lpha_B}$$
,注意到 $|m{r}|^2=m{r}^\daggerm{r}=m{r}^Tm{r}$,因此两边对 $m{r}$ 求导,得:

$$-\alpha_{A}(\mathbf{r} - \mathbf{R}_{A})^{T} - \alpha_{B}(\mathbf{r} - \mathbf{R}_{B})^{T} = -(\alpha_{A} + \alpha_{B})(\mathbf{r} - \mathbf{R}_{P})^{T}$$

$$\Rightarrow -\alpha_{A}(\mathbf{r} - \mathbf{R}_{A})^{T} - \alpha_{B}(\mathbf{r} - \mathbf{R}_{B})^{T} = -(\alpha_{A} + \alpha_{B})(\mathbf{r} - \frac{\alpha_{A}\mathbf{R}_{A} + \alpha_{B}\mathbf{R}_{B}}{\alpha_{A} + \alpha_{B}})^{T}$$

$$\Rightarrow -(\alpha_{A}\mathbf{r} - \alpha_{A}\mathbf{R}_{A})^{T} - (\alpha_{B}\mathbf{r} - \alpha_{B}\mathbf{R}_{B})^{T} = -[(\alpha_{A} + \alpha_{B})\mathbf{r} - (\alpha_{A}\mathbf{R}_{A} + \alpha_{B}\mathbf{R}_{B})]^{T}$$

$$\Rightarrow -[(\alpha_{A} + \alpha_{B})\mathbf{r} - (\alpha_{A}\mathbf{R}_{A} + \alpha_{B}\mathbf{R}_{B})]^{T} = -[(\alpha_{A} + \alpha_{B})\mathbf{r} - (\alpha_{A}\mathbf{R}_{A} + \alpha_{B}\mathbf{R}_{B})]^{T}$$

从而
$$m{R}_P = rac{lpha_A m{R}_A + lpha_B m{R}_B}{lpha_A + lpha_B}$$
时,两边导数相等,而 $r = 0$ 时,代回求导前的等式,得左边为 $-lpha_A |m{R}_A|^2 - lpha_B |m{R}_B|^2 + rac{lpha_A lpha_B}{lpha_A + lpha_B} |m{R}_A - m{R}_B|^2$,右边为 $-(lpha_A + lpha_B) |m{R}_P|^2$,或写作 $-(lpha_A + lpha_B) |rac{lpha_A m{R}_A + lpha_B m{R}_B}{lpha_A + lpha_B}|^2$,而

$$-(\alpha_{A} + \alpha_{B})\left|\frac{\alpha_{A}\mathbf{R}_{A} + \alpha_{B}\mathbf{R}_{B}}{\alpha_{A} + \alpha_{B}}\right|^{2} = -\frac{\left|\alpha_{A}\mathbf{R}_{A} + \alpha_{B}\mathbf{R}_{B}\right|^{2}}{\alpha_{A} + \alpha_{B}} = -\frac{\alpha_{A}^{2}\left|\mathbf{R}_{A}\right|^{2} + \alpha_{B}^{2}\left|\mathbf{R}_{B}\right|^{2} + \alpha_{A}\alpha_{B}\left(\mathbf{R}_{A}^{T}\mathbf{R}_{B} + \mathbf{R}_{B}^{T}\mathbf{R}_{A}\right)}{\alpha_{A} + \alpha_{B}}$$

$$= -\frac{\alpha_{A}(\alpha_{A} + \alpha_{B})\left|\mathbf{R}_{A}\right|^{2} + \alpha_{B}(\alpha_{A} + \alpha_{B})\left|\mathbf{R}_{B}\right|^{2} + \alpha_{A}\alpha_{B}\left(-\left|\mathbf{R}_{A}\right|^{2} + \mathbf{R}_{A}^{T}\mathbf{R}_{B} + \mathbf{R}_{B}^{T}\mathbf{R}_{A} - \left|\mathbf{R}_{B}\right|^{2}\right)}{\alpha_{A} + \alpha_{B}}$$

$$= -\alpha_{A}\left|\mathbf{R}_{A}\right|^{2} - \alpha_{B}\left|\mathbf{R}_{B}\right|^{2} + \frac{\alpha_{A}\alpha_{B}}{\alpha_{A} + \alpha_{B}}\left|\mathbf{R}_{A} - \mathbf{R}_{B}\right|^{2}$$

因此求导前的等式成立, 从而原题得证