课堂练习

练习1：证明$\langle 0|\hat{H}|2\bar{2}\rangle = \langle 1\bar{1}||2\bar{2}\rangle = K_{12}$，其中$|0\rangle \equiv |1\bar{1}\rangle$

证明：根据Slater-Condon规则，我们有：

$$\langle 0|\hat{H}|2\bar{2}\rangle = \langle 1\bar{1}|\hat{H}|2\bar{2}\rangle = \langle 1\bar{1}||2\bar{2}\rangle = \langle 1\bar{1}|2\bar{2}\rangle - \langle 1\bar{1}|\bar{2}2\rangle = \langle 11|22\rangle$$

在空间轨道为实函数的情况下，有$\langle 0|\hat{H}|2\bar{2}\rangle = \langle 11|22\rangle = \langle 12|21\rangle = K_{12}$（实际上，即使空间轨道为复函数，一样有交换积分为实数的结论，从而有$\langle 0|\hat{H}|2\bar{2}\rangle = \langle 11|22\rangle = K_{12}$）

练习2：证明若采用Full CI，则在H_2解离极限下，有$E_0 \xrightarrow{R\to\infty} 2E_H$，相应的波函数为

$$|\Psi_0\rangle \xrightarrow{R\to\infty} \frac{1}{2}[\phi_a(1)\phi_b(2) + \phi_b(1)\phi_a(2)][\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

证明：由Full CI可得H_2基态能量为

$$E_0 = E_0^{(\mathrm{HF})} + E_{corr} = 2h_{11} + J_{11} + \Delta - \sqrt{\Delta^2 + K_{12}^2}$$

其中Δ被定义为

$$\Delta \equiv \frac{1}{2}\langle 2\bar{2}|\hat{H} - E_0|2\bar{2}\rangle = h_{22} - h_{11} + \frac{1}{2}(J_{22} - J_{11})$$

因此代入基态能量的表达式，得

$$\begin{aligned} E_0 &= 2h_{11} + J_{11} + [h_{22} - h_{11} + \frac{1}{2}(J_{22} - J_{11})] - \sqrt{[h_{22} - h_{11} + \frac{1}{2}(J_{22} - J_{11})]^2 + K_{12}^2} \\ &= h_{11} + h_{22} + \frac{1}{2}(J_{11} + J_{22}) - \sqrt{[h_{22} - h_{11} + \frac{1}{2}(J_{22} - J_{11})]^2 + K_{12}^2} \end{aligned}$$

而$\begin{cases} \psi_1(1) = [2(1+S)]^{-\frac{1}{2}}[\phi_a(1) + \phi_b(1)] \\ \psi_2(1) = [2(1-S)]^{-\frac{1}{2}}[\phi_a(1) - \phi_b(1)] \end{cases}$，当$R \to \infty$时，有$S = \int \phi_a^*(\boldsymbol{r}_1)\phi_b(\boldsymbol{r}_1)d\boldsymbol{r}_1 \to 0$，此时$\psi_1(1) \to \frac{\phi_a(1)+\phi_b(1)}{\sqrt{2}}$，$\psi_2(1) \to \frac{\phi_a(1)-\phi_b(1)}{\sqrt{2}}$，因此定义$U = \int |\phi_a(\boldsymbol{r}_1)|^2 \boldsymbol{r}_{12}^{-1} |\phi_a(\boldsymbol{r}_2)|^2 d\boldsymbol{r}_1 d\boldsymbol{r}_2$（由于同核的关系，亦可写作$U = \int |\phi_b(\boldsymbol{r}_1)|^2 \boldsymbol{r}_{12}^{-1} |\phi_b(\boldsymbol{r}_2)|^2 d\boldsymbol{r}_1 d\boldsymbol{r}_2$），则（利用重叠积分趋近于0，以及两个氢原子相距无穷大的条件）

$$\begin{aligned} J_{11} &= \int \psi_1^*(\boldsymbol{r}_1)\psi_1^*(\boldsymbol{r}_2)\boldsymbol{r}_{12}^{-1}\psi_1(\boldsymbol{r}_1)\psi_1(\boldsymbol{r}_2)d\boldsymbol{r}_1 d\boldsymbol{r}_2 \\ &= \frac{1}{4}\int \frac{[\phi_a^*(\boldsymbol{r}_1) + \phi_b^*(\boldsymbol{r}_1)][\phi_a^*(\boldsymbol{r}_2) + \phi_b^*(\boldsymbol{r}_2)][\phi_a(\boldsymbol{r}_1) + \phi_b(\boldsymbol{r}_1)][\phi_a(\boldsymbol{r}_2) + \phi_b(\boldsymbol{r}_2)]}{\boldsymbol{r}_{12}} d\boldsymbol{r}_1 d\boldsymbol{r}_2 \\ &= \frac{1}{4}\int \frac{[\phi_a^*(\boldsymbol{r}_1)\phi_a(\boldsymbol{r}_1) + \phi_b^*(\boldsymbol{r}_1)\phi_b(\boldsymbol{r}_1)][\phi_a^*(\boldsymbol{r}_2)\phi_a(\boldsymbol{r}_2) + \phi_b^*(\boldsymbol{r}_2)\phi_b(\boldsymbol{r}_2)]}{\boldsymbol{r}_{12}} d\boldsymbol{r}_1 d\boldsymbol{r}_2 \\ &= \frac{1}{4}\int \frac{\phi_a^*(\boldsymbol{r}_1)\phi_a(\boldsymbol{r}_1)\phi_a^*(\boldsymbol{r}_2)\phi_a(\boldsymbol{r}_2) + \phi_b^*(\boldsymbol{r}_1)\phi_b(\boldsymbol{r}_1)\phi_b^*(\boldsymbol{r}_2)\phi_b(\boldsymbol{r}_2)}{\boldsymbol{r}_{12}} d\boldsymbol{r}_1 d\boldsymbol{r}_2 = \frac{U}{2} \end{aligned}$$

$$
\begin{aligned}
J_{22} &= \int \psi_2^*(\boldsymbol{r}_1)\psi_2^*(\boldsymbol{r}_2)\boldsymbol{r}_{12}^{-1}\psi_2(\boldsymbol{r}_1)\psi_2(\boldsymbol{r}_2)d\boldsymbol{r}_1 d\boldsymbol{r}_2 \\
&= \frac{1}{4}\int \frac{[\phi_a^*(\boldsymbol{r}_1)-\phi_b^*(\boldsymbol{r}_1)][\phi_a^*(\boldsymbol{r}_2)-\phi_b^*(\boldsymbol{r}_2)][\phi_a(\boldsymbol{r}_1)-\phi_b(\boldsymbol{r}_1)][\phi_a(\boldsymbol{r}_2)-\phi_b(\boldsymbol{r}_2)]}{\boldsymbol{r}_{12}} d\boldsymbol{r}_1 d\boldsymbol{r}_2 \\
&= \frac{1}{4}\int \frac{[\phi_a^*(\boldsymbol{r}_1)\phi_a(\boldsymbol{r}_1)+\phi_b^*(\boldsymbol{r}_1)\phi_b(\boldsymbol{r}_1)][\phi_a^*(\boldsymbol{r}_2)\phi_a(\boldsymbol{r}_2)+\phi_b^*(\boldsymbol{r}_2)\phi_b(\boldsymbol{r}_2)]}{\boldsymbol{r}_{12}} d\boldsymbol{r}_1 d\boldsymbol{r}_2 \\
&= \frac{1}{4}\int \frac{\phi_a^*(\boldsymbol{r}_1)\phi_a(\boldsymbol{r}_1)\phi_a^*(\boldsymbol{r}_2)\phi_a(\boldsymbol{r}_2)+\phi_b^*(\boldsymbol{r}_1)\phi_b(\boldsymbol{r}_1)\phi_b^*(\boldsymbol{r}_2)\phi_b(\boldsymbol{r}_2)}{\boldsymbol{r}_{12}} d\boldsymbol{r}_1 d\boldsymbol{r}_2 = \frac{U}{2}
\end{aligned}
$$

$$
\begin{aligned}
K_{12} &= \int \psi_1^*(\boldsymbol{r}_1)\psi_2^*(\boldsymbol{r}_2)\boldsymbol{r}_{12}^{-1}\psi_2(\boldsymbol{r}_1)\psi_1(\boldsymbol{r}_2)d\boldsymbol{r}_1 d\boldsymbol{r}_2 \\
&= \frac{1}{4}\int \frac{[\phi_a^*(\boldsymbol{r}_1)+\phi_b^*(\boldsymbol{r}_1)][\phi_a^*(\boldsymbol{r}_2)-\phi_b^*(\boldsymbol{r}_2)][\phi_a(\boldsymbol{r}_1)-\phi_b(\boldsymbol{r}_1)][\phi_a(\boldsymbol{r}_2)+\phi_b(\boldsymbol{r}_2)]}{\boldsymbol{r}_{12}} d\boldsymbol{r}_1 d\boldsymbol{r}_2 \\
&= \frac{1}{4}\int \frac{[\phi_a^*(\boldsymbol{r}_1)\phi_a(\boldsymbol{r}_1)-\phi_b^*(\boldsymbol{r}_1)\phi_b(\boldsymbol{r}_1)][\phi_a^*(\boldsymbol{r}_2)\phi_a(\boldsymbol{r}_2)-\phi_b^*(\boldsymbol{r}_2)\phi_b(\boldsymbol{r}_2)]}{\boldsymbol{r}_{12}} d\boldsymbol{r}_1 d\boldsymbol{r}_2 \\
&= \frac{1}{4}\int \frac{\phi_a^*(\boldsymbol{r}_1)\phi_a(\boldsymbol{r}_1)\phi_a^*(\boldsymbol{r}_2)\phi_a(\boldsymbol{r}_2)+\phi_b^*(\boldsymbol{r}_1)\phi_b(\boldsymbol{r}_1)\phi_b^*(\boldsymbol{r}_2)\phi_b(\boldsymbol{r}_2)}{\boldsymbol{r}_{12}} d\boldsymbol{r}_1 d\boldsymbol{r}_2 = \frac{U}{2}
\end{aligned}
$$

又知道单个氢原子的能量为$E_H \equiv h_{11} = h_{22}$，故代入得$E_0 = 2E_H$，$E_{corr} = -K_{12}$，而Full CI下$H_2$的波函数为$|\Psi\rangle = |1\bar{1}\rangle + c|2\bar{2}\rangle$，系数$c$满足$c = \frac{E_{corr}}{K_{12}}$，故回代得$c = -1$，从而在解离极限下，$H_2$的波函数为（存疑）

$$
\begin{aligned}
&|\Psi\rangle = |1\bar{1}\rangle - |2\bar{2}\rangle \\
&= \frac{1}{\sqrt{2!}}[\psi_1(\boldsymbol{r}_1)\alpha(s_1)\psi_1(\boldsymbol{r}_2)\beta(s_2) - \psi_1(\boldsymbol{r}_1)\beta(s_1)\psi_1(\boldsymbol{r}_2)\alpha(s_2)] \\
&\quad - \frac{1}{\sqrt{2!}}[\psi_2(\boldsymbol{r}_1)\alpha(s_1)\psi_2(\boldsymbol{r}_2)\beta(s_2) - \psi_2(\boldsymbol{r}_1)\beta(s_1)\psi_2(\boldsymbol{r}_2)\alpha(s_2)] \\
&= \frac{\psi_1(\boldsymbol{r}_1)\psi_1(\boldsymbol{r}_2)}{\sqrt{2}}[\alpha(s_1)\beta(s_2)-\beta(s_1)\alpha(s_2)] - \frac{\psi_2(\boldsymbol{r}_1)\psi_2(\boldsymbol{r}_2)}{\sqrt{2}}[\alpha(s_1)\beta(s_2)-\beta(s_1)\alpha(s_2)] \\
&= \frac{1}{\sqrt{2}}[\psi_1(\boldsymbol{r}_1)\psi_1(\boldsymbol{r}_2) - \psi_2(\boldsymbol{r}_1)\psi_2(\boldsymbol{r}_2)][\alpha(s_1)\beta(s_2)-\beta(s_1)\alpha(s_2)] \\
&= \frac{1}{\sqrt{2}}[\frac{\phi_a(\boldsymbol{r}_1)+\phi_b(\boldsymbol{r}_1)}{\sqrt{2}}\frac{\phi_a(\boldsymbol{r}_2)+\phi_b(\boldsymbol{r}_2)}{\sqrt{2}} - \frac{\phi_a(\boldsymbol{r}_1)-\phi_b(\boldsymbol{r}_1)}{\sqrt{2}}\frac{\phi_a(\boldsymbol{r}_2)-\phi_b(\boldsymbol{r}_2)}{\sqrt{2}}][\alpha(s_1)\beta(s_2)-\beta(s_1)\alpha(s_2)] \\
&= \frac{1}{\sqrt{2}}[\phi_a(\boldsymbol{r}_1)\phi_b(\boldsymbol{r}_2)+\phi_b(\boldsymbol{r}_1)\phi_a(\boldsymbol{r}_2)][\alpha(s_1)\beta(s_2)-\beta(s_1)\alpha(s_2)]
\end{aligned}
$$

如果将该波函数重新归一化，便得到本题待证明的等式，证毕

练习3：推导CID方法中相关能的迭代式$E_{corr} = \boldsymbol{b}^\dagger[E_{corr}\boldsymbol{1} - \boldsymbol{D}]^{-1}\boldsymbol{b}$

解：利用CID方法，我们得到矩阵方程为$\begin{pmatrix} 0 & \boldsymbol{b}^\dagger \\ \boldsymbol{b} & \boldsymbol{D} \end{pmatrix}\begin{pmatrix} 1 \\ \boldsymbol{c} \end{pmatrix} = E_{corr}\begin{pmatrix} 1 \\ \boldsymbol{c} \end{pmatrix}$，化成方程式形式为$\begin{cases} \boldsymbol{b}^\dagger\boldsymbol{c} = E_{corr} \\ \boldsymbol{b} + \boldsymbol{D}\boldsymbol{c} = E_{corr}\boldsymbol{c} \end{cases}$，由第二个方程可得$\boldsymbol{b} = (E_{corr}\boldsymbol{1} - \boldsymbol{D})\boldsymbol{c}$，即$\boldsymbol{c} = [E_{corr}\boldsymbol{1} - \boldsymbol{D}]^{-1}\boldsymbol{b}$，代回第一个方程，得$E_{corr} = \boldsymbol{b}^\dagger\boldsymbol{c} = \boldsymbol{b}^\dagger[E_{corr}\boldsymbol{1} - \boldsymbol{D}]^{-1}\boldsymbol{b}$

练习4：在CID方法中，相关能最终的表达式为

$$
E_{corr} = -\sum_{a<b,r<s}\frac{\langle\Phi_0|\hat{H}|\Phi_{ab}^{rs}\rangle\langle\Phi_{ab}^{rs}|\hat{H}|\Phi_0\rangle}{\langle\Phi_{ab}^{rs}|\hat{H} - E_0^{(\mathrm{HF})}|\Phi_{ab}^{rs}\rangle}
$$

证明上式在一定的条件下可以近似为$E_{corr} = \sum_{a<b,r<s}\frac{|\langle ab||rs\rangle|^2}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}$

证明：首先对分子运用Slater-Condon规则，得$\langle\Phi_0|\hat{H}|\Phi_{ab}^{rs}\rangle=\langle ab||rs\rangle$，$\langle\Phi_{ab}^{rs}|\hat{H}|\Phi_0\rangle=\langle rs||ab\rangle$，因此$\langle\Phi_0|\hat{H}|\Phi_{ab}^{rs}\rangle\langle\Phi_{ab}^{rs}|\hat{H}|\Phi_0\rangle=|\langle ab||rs\rangle|^2$；接下来讨论分母这一项，展开后可以得到

$$\langle\Phi_{ab}^{rs}|\hat{H}-E_0^{(\mathrm{HF})}|\Phi_{ab}^{rs}\rangle=h_{rr}+h_{ss}-h_{aa}-h_{bb}+\frac{1}{2}\sum_{i,j\neq a,b}\langle ij||ij\rangle-\frac{1}{2}\sum_{i,j\neq r,s}\langle ij||ij\rangle$$

$$=h_{rr}+h_{ss}-h_{aa}-h_{bb}+\frac{1}{2}\sum_{j\neq a,b}(\langle rj||rj\rangle+\langle sj||sj\rangle)+\frac{1}{2}\sum_{i\neq a,b}(\langle ir||ir\rangle+\langle is||is\rangle)$$

$$-\frac{1}{2}\sum_{j\neq r,s}(\langle aj||aj\rangle+\langle bj||bj\rangle)-\frac{1}{2}\sum_{i\neq r,s}(\langle ia||ia\rangle+\langle ib||ib\rangle)$$

而对于任意轨道，有$\varepsilon_i=h_{ii}+\sum\limits_j\langle ij||ij\rangle$，因此可化简为

$$\begin{aligned}\langle\Phi_{ab}^{rs}|\hat{H}-E_0^{(\mathrm{HF})}|\Phi_{ab}^{rs}\rangle&=(h_{rr}+\frac{1}{2}\sum_{j\neq a,b}\langle rj||rj\rangle+\frac{1}{2}\sum_{i\neq a,b}\langle ir||ir\rangle)+(h_{ss}+\frac{1}{2}\sum_{j\neq a,b}\langle sj||sj\rangle+\frac{1}{2}\sum_{i\neq a,b}\langle is||is\rangle)\\&\quad-(h_{aa}+\frac{1}{2}\sum_{j\neq r,s}\langle aj||aj\rangle+\frac{1}{2}\sum_{i\neq r,s}\langle ia||ia\rangle)-(h_{bb}+\frac{1}{2}\sum_{j\neq r,s}\langle bj||bj\rangle+\frac{1}{2}\sum_{i\neq r,s}\langle ib||ib\rangle)\\&=(h_{rr}+\sum_{j\neq a,b}\langle rj||rj\rangle)+(h_{ss}+\sum_{j\neq a,b}\langle sj||sj\rangle)-(h_{aa}+\sum_{j\neq r,s}\langle aj||aj\rangle)-(h_{bb}+\sum_{j\neq r,s}\langle bj||bj\rangle)\\&=(h_{rr}+\sum_{j}\langle rj||rj\rangle)+(h_{ss}+\sum_{j}\langle sj||sj\rangle)-(h_{aa}+\sum_{j}\langle aj||aj\rangle)-(h_{bb}+\sum_{j}\langle bj||bj\rangle)\\&\quad-(\langle ra||ra\rangle+\langle rb||rb\rangle)-(\langle sa||sa\rangle+\langle sb||sb\rangle)+(\langle ar||ar\rangle+\langle as||as\rangle)+(\langle br||br\rangle+\langle bs||bs\rangle)\\&\approx\varepsilon_r+\varepsilon_s-\varepsilon_a-\varepsilon_b\text{（后四项相互抵消）}\end{aligned}$$

最后代入，即可得$E_{corr}=-\sum\limits_{a<b,r<s}\frac{|\langle ab||rs\rangle|^2}{\varepsilon_r+\varepsilon_s-\varepsilon_a-\varepsilon_b}=\sum\limits_{a<b,r<s}\frac{|\langle ab||rs\rangle|^2}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}$

练习5：在双氢分子模型中，记波函数为$|\Phi_0\rangle=|1_1\bar{1}_11_2\bar{1}_2\rangle$，$|\Phi_1\rangle=|\Phi_{1_2\bar{1}_2}^{2_2\bar{2}_2}\rangle=|1_1\bar{1}_12_2\bar{2}_2\rangle$，$|\Phi_2\rangle=|\Phi_{1_1\bar{1}_1}^{2_1\bar{2}_1}\rangle=|2_1\bar{2}_11_2\bar{1}_2\rangle$，试推导$\langle\Phi_0|\hat{H}|\Phi_1\rangle=\langle\Phi_0|\hat{H}|\Phi_2\rangle=K_{12}$，$\langle\Phi_1|(\hat{H}-E_0^{(\mathrm{HF})})|\Phi_1\rangle=\langle\Phi_2|(\hat{H}-E_0^{(\mathrm{HF})})|\Phi_2\rangle=2\Delta$（$\Delta$的定义见练习2）

解：根据Slater-Condon规则，我们有：

$$\begin{aligned}\langle\Phi_0|\hat{H}|\Phi_1\rangle&=\langle1_1\bar{1}_11_2\bar{1}_2|\hat{H}|1_1\bar{1}_12_2\bar{2}_2\rangle=\langle1_1\bar{1}_11_2\bar{1}_2||1_1\bar{1}_12_2\bar{2}_2\rangle=\langle1_1\bar{1}_11_2\bar{1}_2|1_1\bar{1}_12_2\bar{2}_2\rangle-\langle1_1\bar{1}_11_2\bar{1}_2|1_1\bar{1}_1\bar{2}_22_2\rangle\\&=\langle1_11_11_21_2|1_11_12_22_2\rangle=K_{12}\end{aligned}$$

$$\begin{aligned}\langle\Phi_0|\hat{H}|\Phi_2\rangle&=\langle1_1\bar{1}_11_2\bar{1}_2|\hat{H}|2_1\bar{2}_11_2\bar{1}_2\rangle=\langle1_1\bar{1}_11_2\bar{1}_2||2_1\bar{2}_11_2\bar{1}_2\rangle=\langle1_1\bar{1}_11_2\bar{1}_2|2_1\bar{2}_11_2\bar{1}_2\rangle-\langle1_1\bar{1}_11_2\bar{1}_2|\bar{2}_12_11_2\bar{1}_2\rangle\\&=\langle1_11_11_21_2|2_12_11_21_2\rangle=K_{12}\end{aligned}$$

同理

$$\begin{aligned}\langle\Phi_1|(\hat{H}-E_0^{(\mathrm{HF})})|\Phi_1\rangle&=\langle1_1\bar{1}_12_2\bar{2}_2|\hat{H}|1_1\bar{1}_12_2\bar{2}_2\rangle-E_0=(2h_{11}+2h_{22}+J_{11}+J_{22})-(4h_{11}+2J_{11})\\&=2h_{22}-2h_{11}+J_{22}-J_{11}=2\Delta\end{aligned}$$

$$\begin{aligned}\langle\Phi_2|(\hat{H}-E_0^{(\mathrm{HF})})|\Phi_2\rangle&=\langle2_1\bar{2}_11_2\bar{1}_2|\hat{H}|2_1\bar{2}_11_2\bar{1}_2\rangle-E_0=(2h_{11}+2h_{22}+J_{11}+J_{22})-(4h_{11}+2J_{11})\\&=2h_{22}-2h_{11}+J_{22}-J_{11}=2\Delta\end{aligned}$$

练习6：对于有N个相距足够远（从而没有相互作用）的H_2分子构成的复合体系，在CID方法下，试证明其相关能为$E_{corr}(N\,\mathrm{H}_2)=\Delta-\sqrt{\Delta^2+NK_{12}^2}$

证明：在CID方法下，记波函数为$|\Psi\rangle=|\Phi_0\rangle+\sum\limits_{i=1}^{N}c_i|\Phi_i\rangle$，其中$|\Phi_0\rangle=|1_1\bar{1}_1\dots1_N\bar{1}_N\rangle$，$|\Phi_i\rangle=|1_1\bar{1}_1\dots2_i\bar{2}_i\dots1_N\bar{1}_N\rangle$，$i=1,2,\dots,N$，则有

$$\begin{cases}\langle\Phi_0|(\hat{H}-E_0^{(\mathrm{HF})})|\Phi_0\rangle=0\\ \langle\Phi_0|(\hat{H}-E_0^{(\mathrm{HF})})|\Phi_i\rangle=\langle\Phi_i|(\hat{H}-E_0^{(\mathrm{HF})})|\Phi_0\rangle=K_{12}\ (i=1,2,\ldots,N)\\ \langle\Phi_i|(\hat{H}-E_0^{(\mathrm{HF})})|\Phi_i\rangle=2\Delta\ (i=1,2,\ldots,N)\\ \langle\Phi_i|(\hat{H}-E_0^{(\mathrm{HF})})|\Phi_j\rangle=\langle\Phi_j|(\hat{H}-E_0^{(\mathrm{HF})})|\Phi_i\rangle=0\ (i,j=1,2,\ldots,N)\end{cases}$$

因此相应的矩阵方程为：

$$\begin{pmatrix}0 & K_{12} & K_{12} & \ldots & K_{12}\\ K_{12} & 2\Delta & 0 & \ldots & 0\\ K_{12} & 0 & 2\Delta & \ldots & 0\\ \vdots & \vdots & \vdots & \ddots & \vdots\\ K_{12} & 0 & 0 & \ldots & 2\Delta\end{pmatrix}\begin{pmatrix}1\\ c_1\\ c_2\\ \vdots\\ c_N\end{pmatrix}=E_{corr}\begin{pmatrix}1\\ c_1\\ c_2\\ \vdots\\ c_N\end{pmatrix}$$

其对应的久期方程为：

$$\begin{vmatrix}-E_{corr} & K_{12} & K_{12} & \ldots & K_{12}\\ K_{12} & 2\Delta-E_{corr} & 0 & \ldots & 0\\ K_{12} & 0 & 2\Delta-E_{corr} & \ldots & 0\\ \vdots & \vdots & \vdots & \ddots & \vdots\\ K_{12} & 0 & 0 & \ldots & 2\Delta-E_{corr}\end{vmatrix}=0$$

经化简可得$[-E_{corr}(2\Delta-E_{corr})-NK_{12}^2](2\Delta-E_{corr})^{N-1}=0$，解得$E_{corr}=2\Delta$或$E_{corr}=\Delta\pm\sqrt{\Delta^2+NK_{12}^2}$，若$E_{corr}=2\Delta$，则代回矩阵方程，得$\begin{cases}-2\Delta+\sum\limits_{i=1}^{N}K_{12}c_i=0\\ K_{12}=0\end{cases}$，而$K_{12}$显然不为0，故该解舍去；若$E_{corr}=\Delta+\sqrt{\Delta^2+NK_{12}^2}$，则代回矩阵方程，得

$$\begin{cases}-\Delta-\sqrt{\Delta^2+NK_{12}^2}+\sum\limits_{i=1}^{N}c_iK_{12}=0\\ K_{12}+(\Delta-\sqrt{\Delta^2+NK_{12}^2})c_i=0\end{cases}\Rightarrow c_i=\frac{-K_{12}}{\Delta-\sqrt{\Delta^2+NK_{12}^2}}=\frac{\Delta+\sqrt{\Delta^2+NK_{12}^2}}{NK_{12}}\ (i=1,2,\ldots,N)$$

若$E_{corr}=\Delta-\sqrt{\Delta^2+NK_{12}^2}$，则代回矩阵方程，得

$$\begin{cases}-\Delta+\sqrt{\Delta^2+NK_{12}^2}+\sum\limits_{i=1}^{N}c_iK_{12}=0\\ K_{12}+(\Delta+\sqrt{\Delta^2+NK_{12}^2})c_i=0\end{cases}\Rightarrow c_i=\frac{-K_{12}}{\Delta+\sqrt{\Delta^2+NK_{12}^2}}=\frac{\Delta-\sqrt{\Delta^2+NK_{12}^2}}{NK_{12}}\ (i=1,2,\ldots,N)$$

对于后HF方法而言，由于HF采用变分法，其得到的能量高于真实能量，因此相关能必然为负，因此$E_{corr}(N\ \mathrm{H}_2)=\Delta-\sqrt{\Delta^2+NK_{12}^2}$，原题得证

练习7：试对双氢分子模型运用Full CI，推导出如下矩阵方程

$$\begin{pmatrix}0 & K_{12} & K_{12} & 0\\ K_{12} & 2\Delta & 0 & K_{12}\\ K_{12} & 0 & 2\Delta & K_{12}\\ 0 & K_{12} & K_{12} & 4\Delta\end{pmatrix}\begin{pmatrix}1\\ c_1\\ c_2\\ c_3\end{pmatrix}=E_{corr}\begin{pmatrix}1\\ c_1\\ c_2\\ c_3\end{pmatrix}$$

由此得到双氢分子的相关能和各个系数的表达式

$$E_{corr}(2\mathrm{H}_2)=2[\Delta-\sqrt{\Delta^2+K_{12}^2}]=2E_{corr}(\mathrm{H}_2)$$

$$c_1=c_2=\frac{\Delta-\sqrt{\Delta^2+K_{12}^2}}{K_{12}}\quad c_3=c_1^2$$

解：设体系全波函数为$|\Psi\rangle=|\Phi_0\rangle+c_1|\Phi_1\rangle+c_2|\Phi_2\rangle+c_3|\Phi_3\rangle$，其中$|\Phi_0\rangle$，$|\Phi_1\rangle$，$|\Phi_2\rangle$的定义见练习5，$|\Phi_3\rangle=|\Phi_{1_1\bar{1}_11_2\bar{1}_2}^{2_1\bar{2}_12_2\bar{2}_2}\rangle=|2_1\bar{2}_12_2\bar{2}_2\rangle$，现在要考虑$\langle\Phi_i|(\hat{H}-E_0^{(\mathrm{HF})})|\Phi_3\rangle$和$\langle\Phi_3|(\hat{H}-E_0^{(\mathrm{HF})})|\Phi_i\rangle$，显然

$$\begin{aligned}
\langle\Phi_0|(\hat{H}-E_0^{(\mathrm{HF})})|\Phi_3\rangle&=\langle\Phi_3|(\hat{H}-E_0^{(\mathrm{HF})})|\Phi_0\rangle=\langle\Phi_0|\hat{H}|\Phi_3\rangle=\langle\Phi_3|\hat{H}|\Phi_0\rangle=0\\
\langle\Phi_1|(\hat{H}-E_0^{(\mathrm{HF})})|\Phi_3\rangle&=\langle\Phi_3|(\hat{H}-E_0^{(\mathrm{HF})})|\Phi_1\rangle=\langle\Phi_1|\hat{H}|\Phi_3\rangle=\langle\Phi_3|\hat{H}|\Phi_1\rangle=\langle1_1\bar{1}_12_2\bar{2}_2|\hat{H}|2_1\bar{2}_12_2\bar{2}_2\rangle\\
&=\langle1_1\bar{1}_12_2\bar{2}_2||2_1\bar{2}_12_2\bar{2}_2\rangle=\langle1_1\bar{1}_12_2\bar{2}_2|2_1\bar{2}_12_2\bar{2}_2\rangle-\langle1_1\bar{1}_12_2\bar{2}_2|\bar{2}_12_12_2\bar{2}_2\rangle=K_{12}\\
\langle\Phi_1|(\hat{H}-E_0^{(\mathrm{HF})})|\Phi_3\rangle&=\langle\Phi_3|(\hat{H}-E_0^{(\mathrm{HF})})|\Phi_1\rangle=\langle\Phi_1|\hat{H}|\Phi_3\rangle=\langle\Phi_3|\hat{H}|\Phi_1\rangle=\langle1_1\bar{1}_12_2\bar{2}_2|\hat{H}|2_1\bar{2}_12_2\bar{2}_2\rangle\\
&=\langle1_1\bar{1}_12_2\bar{2}_2||2_1\bar{2}_12_2\bar{2}_2\rangle=\langle1_1\bar{1}_12_2\bar{2}_2|2_1\bar{2}_12_2\bar{2}_2\rangle-\langle1_1\bar{1}_12_2\bar{2}_2|\bar{2}_12_12_2\bar{2}_2\rangle=K_{12}\\
\langle\Phi_3|(\hat{H}-E_0^{(\mathrm{HF})})|\Phi_3\rangle&=\langle\Phi_3|\hat{H}|\Phi_3\rangle-E_0^{(\mathrm{HF})}=\langle2_1\bar{2}_12_2\bar{2}_2|\hat{H}|2_1\bar{2}_12_2\bar{2}_2\rangle-E_0^{(\mathrm{HF})}\\
&=4h_{22}+2J_{22}-4h_{11}-2J_{11}=4\Delta
\end{aligned}$$

因此对$(\hat{H}-E_0^{(\mathrm{HF})})|\Psi\rangle=E_{corr}|\Psi\rangle$分别左乘$|\Phi_0\rangle$，$|\Phi_1\rangle$，$|\Phi_2\rangle$，$|\Phi_3\rangle$，结合练习5的结论，得如下矩阵方程

$$\begin{pmatrix}0&K_{12}&K_{12}&0\\K_{12}&2\Delta&0&K_{12}\\K_{12}&0&2\Delta&K_{12}\\0&K_{12}&K_{12}&4\Delta\end{pmatrix}\begin{pmatrix}1\\c_1\\c_2\\c_3\end{pmatrix}=E_{corr}\begin{pmatrix}1\\c_1\\c_2\\c_3\end{pmatrix}$$

相应的久期方程为

$$\begin{vmatrix}-E_{corr}&K_{12}&K_{12}&0\\K_{12}&2\Delta-E_{corr}&0&K_{12}\\K_{12}&0&2\Delta-E_{corr}&K_{12}\\0&K_{12}&K_{12}&4\Delta-E_{corr}\end{vmatrix}=0$$

经化简可得$(2\Delta-E_{corr})^2[E_{corr}^2-(4\Delta)E_{corr}-4K_{12}^2]=0$，解得$E_{corr}=2\Delta$或$E_{corr}=2\Delta\pm2\sqrt{\Delta^2+K_{12}^2}$。

若$E_{corr}=2\Delta$，代入矩阵方程得$\begin{cases}-2\Delta+K_{12}(c_1+c_2)=0\\K_{12}+K_{12}c_3=0\\K_{12}(c_1+c_2)+(2\Delta)c_3=0\end{cases}$，解得$\begin{cases}c_1+c_2=\frac{2\Delta}{K_{12}}\\c_3=-1\end{cases}$

若$E_{corr}=2\Delta+2\sqrt{\Delta^2+K_{12}^2}$，代入矩阵方程得

$$\begin{cases}-2\Delta-2\sqrt{\Delta^2+K_{12}^2}+K_{12}(c_1+c_2)=0\\K_{12}-2\sqrt{\Delta^2+K_{12}^2}c_1+K_{12}c_3=0\\K_{12}-2\sqrt{\Delta^2+K_{12}^2}c_2+K_{12}c_3=0\\K_{12}(c_1+c_2)+(2\Delta-2\sqrt{\Delta^2+K_{12}^2})c_3=0\end{cases}$$

解得$\begin{cases}c_1=c_2=\frac{\Delta+\sqrt{\Delta^2+K_{12}^2}}{K_{12}}\\c_3=\frac{\Delta+\sqrt{\Delta^2+K_{12}^2}}{\Delta-\sqrt{\Delta^2+K_{12}^2}}=-\frac{(\Delta+\sqrt{\Delta^2+K_{12}^2})^2}{K_{12}^2}=-c_1^2\end{cases}$

若$E_{corr}=2\Delta-2\sqrt{\Delta^2+K_{12}^2}$，代入矩阵方程得

$$\begin{cases} -2\Delta + 2\sqrt{\Delta^2 + K_{12}^2} + K_{12}(c_1 + c_2) = 0 \\ K_{12} + 2\sqrt{\Delta^2 + K_{12}^2}c_1 + K_{12}c_3 = 0 \\ K_{12} + 2\sqrt{\Delta^2 + K_{12}^2}c_2 + K_{12}c_3 = 0 \\ K_{12}(c_1 + c_2) + (2\Delta + 2\sqrt{\Delta^2 + K_{12}^2})c_3 = 0 \end{cases}$$

解得$\begin{cases} c_1 = c_2 = \frac{\Delta - \sqrt{\Delta^2 + K_{12}^2}}{K_{12}} \\ c_3 = -\frac{\Delta - \sqrt{\Delta^2 + K_{12}^2}}{\Delta + \sqrt{\Delta^2 + K_{12}^2}} = \frac{(\Delta - \sqrt{\Delta^2 + K_{12}^2})^2}{K_{12}^2} = c_1^2 \end{cases}$

对于后HF方法而言，由于HF采用变分法，其得到的能量高于真实能量，因此相关能必然为负，从而符合条件的解为$E_{corr}(2\mathrm{H}_2) = 2\Delta - 2\sqrt{\Delta^2 + K_{12}^2} = 2E_{corr}(\mathrm{H}_2)$，$c_1 = c_2 = \frac{\Delta - \sqrt{\Delta^2 + K_{12}^2}}{K_{12}}$，$c_3 = c_1^2$。