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）

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

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

$$
E_{corr} = -\sum_{a<b,r<s}\frac{\langle\Psi_0|\hat{H}|\Psi_{ab}^{rs}\rangle\langle\Psi_{ab}^{rs}|\hat{H}|\Psi_0\rangle}{\langle\Psi_{ab}^{rs}|\hat{H} - E_0^{(\mathrm{HF})}|\Psi_{ab}^{rs}\rangle}
$$

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：

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

解：根据Slater-Condon规则，我们有：

$$\langle\Phi_0|\hat{H}|\Phi_1\rangle = \langle 1_1\bar{1}_1 1_2\bar{1}_2|\hat{H}|2_1\bar{2}_1 1_2\bar{1}_2\rangle = \langle 1_1\bar{1}_1 1_2\bar{1}_2||2_1\bar{2}_1 1_2\bar{1}_2\rangle$$

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$|\Phi_0\rangle = |1_1\bar{1}_1 \dots 1_N\bar{1}_N\rangle$，$|\Phi_i\rangle = |1_1\bar{1}_1 \dots 2_i\bar{2}_i \dots 1_N\bar{1}_N\rangle$，$i = 1, 2, \dots, N$，则有

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

因此相应的矩阵方程为：

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

其对应的久期方程为：

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

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$E_{corr} = \Delta + \sqrt{\Delta^2 + NK_{12}^2}$，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

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

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: