课堂练习

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

证明:根据Slater-Condon规则,我们有:

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

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 ${ m H_2}$ 解离极限下,有 $E_0 \stackrel{R o \infty}{-\!\!\!\!-\!\!\!\!-\!\!\!\!-\!\!\!\!-} 2E_H$,相应的波函数为

$$|\Psi_0
angle \xrightarrow{R o\infty} rac{1}{2} [\phi_a(1)\phi_b(2) + \phi_b(1)\phi_a(2)] [lpha(1)eta(2) - lpha(2)eta(1)]$$

证明:由Full CI可得H2基态能量为

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

其中△被定义为

$$\Delta \equiv rac{1}{2} \langle 2ar{2}|\hat{H} - E_0|2ar{2}
angle = h_{22} - h_{11} + rac{1}{2}(J_{22} - J_{11})$$

因此代入基态能量的表达式,得

$$E_0 = 2h_{11} + J_{11} + [h_{22} - h_{11} + rac{1}{2}(J_{22} - J_{11})] - \sqrt{[h_{22} - h_{11} + rac{1}{2}(J_{22} - J_{11})]^2 + K_{12}^2} \ = h_{11} + h_{22} + rac{1}{2}(J_{11} + J_{22}) - \sqrt{[h_{22} - h_{11} + rac{1}{2}(J_{22} - J_{11})]^2 + K_{12}^2}$$

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

$$egin{aligned} J_{11} &= \int \psi_1^*(m{r}_1) \psi_1^*(m{r}_2) m{r}_{12}^{-1} \psi_1(m{r}_1) \psi_1(m{r}_2) dm{r}_1 dm{r}_2 \ &= rac{1}{4} \int rac{[\phi_a^*(m{r}_1) + \phi_b^*(m{r}_1)][\phi_a^*(m{r}_2) + \phi_b^*(m{r}_2)][\phi_a(m{r}_1) + \phi_b(m{r}_1)][\phi_a(m{r}_2) + \phi_b(m{r}_2)]}{m{r}_{12}} dm{r}_1 dm{r}_2 \ &= rac{1}{4} \int rac{[\phi_a^*(m{r}_1)\phi_a(m{r}_1) + \phi_b^*(m{r}_1)\phi_b(m{r}_1)][\phi_a^*(m{r}_2)\phi_a(m{r}_2) + \phi_b^*(m{r}_2)\phi_b(m{r}_2)]}{m{r}_{12}} dm{r}_1 dm{r}_2 \ &= rac{1}{4} \int rac{\phi_a^*(m{r}_1)\phi_a(m{r}_1)\phi_a^*(m{r}_2)\phi_a(m{r}_2) + \phi_b^*(m{r}_1)\phi_b(m{r}_1)\phi_b^*(m{r}_2)\phi_b(m{r}_2)}{m{r}_{12}} dm{r}_1 dm{r}_2 = rac{U}{2} \end{aligned}$$

$$\begin{split} &=\frac{1}{4}\int\frac{[\phi_a^*(\boldsymbol{r}_1)-\phi_b^*(\boldsymbol{r}_1)][\phi_a^*(\boldsymbol{r}_2)-\phi_b^*(\boldsymbol{r}_2)][\phi_a(\boldsymbol{r}_1)-\phi_b(\boldsymbol{r}_1)][\phi_a(\boldsymbol{r}_2)-\phi_b(\boldsymbol{r}_2)]}{\boldsymbol{r}_{12}}d\boldsymbol{r}_1d\boldsymbol{r}_2}{=\frac{1}{4}\int\frac{[\phi_a^*(\boldsymbol{r}_1)\phi_a(\boldsymbol{r}_1)+\phi_b^*(\boldsymbol{r}_1)\phi_b(\boldsymbol{r}_1)][\phi_a^*(\boldsymbol{r}_2)\phi_a(\boldsymbol{r}_2)+\phi_b^*(\boldsymbol{r}_2)\phi_b(\boldsymbol{r}_2)]}{\boldsymbol{r}_{12}}d\boldsymbol{r}_1d\boldsymbol{r}_2}{=\frac{1}{4}\int\frac{\phi_a^*(\boldsymbol{r}_1)\phi_a(\boldsymbol{r}_1)\phi_a^*(\boldsymbol{r}_2)\phi_a(\boldsymbol{r}_2)+\phi_b^*(\boldsymbol{r}_1)\phi_b(\boldsymbol{r}_1)\phi_b^*(\boldsymbol{r}_2)\phi_b(\boldsymbol{r}_2)}{\boldsymbol{r}_{12}}d\boldsymbol{r}_1d\boldsymbol{r}_2=\frac{U}{2}}\\ K_{12}&=\int\psi_1^*(\boldsymbol{r}_1)\psi_2^*(\boldsymbol{r}_2)\boldsymbol{r}_{12}^{-1}\psi_2(\boldsymbol{r}_1)\psi_1(\boldsymbol{r}_2)d\boldsymbol{r}_1d\boldsymbol{r}_2}{=\frac{1}{4}\int\frac{[\phi_a^*(\boldsymbol{r}_1)+\phi_b^*(\boldsymbol{r}_1)][\phi_a^*(\boldsymbol{r}_2)-\phi_b^*(\boldsymbol{r}_2)][\phi_a(\boldsymbol{r}_1)-\phi_b(\boldsymbol{r}_1)][\phi_a(\boldsymbol{r}_2)+\phi_b(\boldsymbol{r}_2)]}{\boldsymbol{r}_{12}}d\boldsymbol{r}_1d\boldsymbol{r}_2}\\ &=\frac{1}{4}\int\frac{[\phi_a^*(\boldsymbol{r}_1)\phi_a(\boldsymbol{r}_1)-\phi_b^*(\boldsymbol{r}_1)\phi_b(\boldsymbol{r}_1)][\phi_a^*(\boldsymbol{r}_2)\phi_a(\boldsymbol{r}_2)-\phi_b^*(\boldsymbol{r}_2)\phi_b(\boldsymbol{r}_2)]}{\boldsymbol{r}_{12}}d\boldsymbol{r}_1d\boldsymbol{r}_2}{=\frac{1}{4}\int\frac{[\phi_a^*(\boldsymbol{r}_1)\phi_a(\boldsymbol{r}_1)\phi_a(\boldsymbol{r}_1)\phi_a^*(\boldsymbol{r}_2)\phi_a(\boldsymbol{r}_2)+\phi_b^*(\boldsymbol{r}_1)\phi_b^*(\boldsymbol{r}_1)\phi_b^*(\boldsymbol{r}_2)\phi_b(\boldsymbol{r}_2)}{\boldsymbol{r}_{12}}d\boldsymbol{r}_1d\boldsymbol{r}_2=\frac{U}{2}}\\ \end{split}$$

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)

$$\begin{split} &|\Psi\rangle = |1\overline{1}\rangle - |2\overline{2}\rangle \\ &= \frac{1}{\sqrt{2!}}[\psi_{1}(\boldsymbol{r}_{1})\alpha(s_{1})\psi_{1}(\boldsymbol{r}_{2})\beta(s_{2}) - \psi_{1}(\boldsymbol{r}_{1})\beta(s_{1})\psi_{1}(\boldsymbol{r}_{2})\alpha(s_{2})] \\ &- \frac{1}{\sqrt{2!}}[\psi_{2}(\boldsymbol{r}_{1})\alpha(s_{1})\psi_{2}(\boldsymbol{r}_{2})\beta(s_{2}) - \psi_{2}(\boldsymbol{r}_{1})\beta(s_{1})\psi_{2}(\boldsymbol{r}_{2})\alpha(s_{2})] \\ &= \frac{\psi_{1}(\boldsymbol{r}_{1})\psi_{1}(\boldsymbol{r}_{2})}{\sqrt{2}}[\alpha(s_{1})\beta(s_{2}) - \beta(s_{1})\alpha(s_{2})] - \frac{\psi_{2}(\boldsymbol{r}_{1})\psi_{2}(\boldsymbol{r}_{2})}{\sqrt{2}}[\alpha(s_{1})\beta(s_{2}) - \beta(s_{1})\alpha(s_{2})] \\ &= \frac{1}{\sqrt{2}}[\psi_{1}(\boldsymbol{r}_{1})\psi_{1}(\boldsymbol{r}_{2}) - \psi_{2}(\boldsymbol{r}_{1})\psi_{2}(\boldsymbol{r}_{2})][\alpha(s_{1})\beta(s_{2}) - \beta(s_{1})\alpha(s_{2})] \\ &= \frac{1}{\sqrt{2}}[\frac{\phi_{a}(\boldsymbol{r}_{1}) + \phi_{b}(\boldsymbol{r}_{1})}{\sqrt{2}}\frac{\phi_{a}(\boldsymbol{r}_{2}) + \phi_{b}(\boldsymbol{r}_{2})}{\sqrt{2}} - \frac{\phi_{a}(\boldsymbol{r}_{1}) - \phi_{b}(\boldsymbol{r}_{1})}{\sqrt{2}}\frac{\phi_{a}(\boldsymbol{r}_{2}) - \phi_{b}(\boldsymbol{r}_{2})}{\sqrt{2}}][\alpha(s_{1})\beta(s_{2}) - \beta(s_{1})\alpha(s_{2})] \\ &= \frac{1}{\sqrt{2}}[\phi_{a}(\boldsymbol{r}_{1})\phi_{b}(\boldsymbol{r}_{2}) + \phi_{b}(\boldsymbol{r}_{1})\phi_{a}(\boldsymbol{r}_{2})][\alpha(s_{1})\beta(s_{2}) - \beta(s_{1})\alpha(s_{2})] \end{split}$$

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

 $J_{22} = \int \psi_2^*(m{r}_1) \psi_2^*(m{r}_2) m{r}_{12}^{-1} \psi_2(m{r}_1) \psi_2(m{r}_2) dm{r}_1 dm{r}_2$

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

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

练习4: 在CID方法中, 相关能最终的表达式为

$$E_{corr} = -\sum_{a < b, r < s} \frac{\langle \Psi_0 | \hat{H} | \Psi^{rs}_{ab} \rangle \langle \Psi^{rs}_{ab} | \hat{H} | \Psi_0 \rangle}{\langle \Psi^{rs}_{ab} | \hat{H} - E^{(\text{HF})}_0 | \Psi^{rs}_{ab} \rangle}$$

证明上式在一定的条件下可以近似为
$$E_{corr} = \sum_{a < b,r < s} rac{|\langle ab||rs
angle|^2}{arepsilon_a + arepsilon_b - arepsilon_r - arepsilon_s}$$

证明:

练习5: 在双氢分子模型中,记波函数为 $|\Phi_0
angle=|1_1ar{1}_11_2ar{1}_2
angle$, $|\Phi_1
angle=|\Phi_{1_2ar{1}_2}^{2_2ar{2}_2}
angle=|1_1ar{1}_12_2ar{2}_2
angle$, $|\Phi_2
angle=|\Phi_{1_1ar{1}_1}^{2_1ar{2}_1}
angle=|2_1ar{2}_11_2ar{1}_2
angle$,试推导 $\langle\Phi_0|\hat{H}|\Phi_1
angle=\langle\Phi_0|\hat{H}|\Phi_2
angle=K_{12}$, $\langle\Phi_1|\hat{H}-E_0^{(\mathrm{HF})}|\Phi_1
angle=\langle\Phi_2|\hat{H}-E_0^{(\mathrm{HF})}|\Phi_2
angle=2\Delta$

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 ${
m H_2}$ 分子构成的复合体系,在CID方法下,试证明其相关能为 $E_{corr}(N~{
m H_2})=\Delta-\sqrt{\Delta^2+NK_{12}^2}$

证明:在CID方法下,记波函数为 $|\Psi
angle=|\Phi_0
angle+\sum\limits_{i=1}^Nc_i|\Phi_i
angle$,其中 $|\Phi_0
angle=|1_1ar{1}_1\dots 1_Nar{1}_N
angle$, $|\Phi_i
angle=|1_1ar{1}_1\dots 2_iar{2}_i\dots 1_Nar{1}_N
angle$, $i=1,2,\dots,N$,则有

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

因此相应的矩阵方程为:

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

其对应的久期方程为:

$$egin{bmatrix} -E_{corr} & K_{12} & K_{12} & \dots & K_{12} \ K_{12} & 2\Delta - E_{corr} & 0 & \dots & 0 \ K_{12} & 0 & 2\Delta - E_{corr} & \dots & 0 \ dots & dots & dots & \ddots & dots \ K_{12} & 0 & 0 & \dots & 2\Delta - E_{corr} \ \end{pmatrix} = 0$$

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

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

练习7: 试对双氢分子模型运用Full CI,推导出如下矩阵方程

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

由此得到双氢分子的相关能和各个系数的表达式

$$egin{align} E_{corr}(2 ext{H}_2) &= 2[\Delta - \sqrt{\Delta^2 + K_{12}^2}] = 2E_{corr}(ext{H}_2) \ & \ c_1 = c_2 = rac{\Delta - \sqrt{\Delta^2 + K_{12}^2}}{K_{12}} \quad c_3 = c_1^2 \ & \ \end{array}$$

解: