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:

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

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} 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} \\ 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_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{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{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{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{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{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}_2) \phi_b(\boldsymbol{r}_2) \phi_b(\boldsymbol{r}_2)$$

又知道单个氢原子的能量为 $E_H\equiv h_{11}=h_{22}$, 故代入得 $E_0=2E_H$

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

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 $\begin{cases} m{b}^\dagger m{c} = E_{corr} \\ m{b} + m{D} m{c} = E_{corr} m{c} \end{cases}$,由第二个方程可得 $m{b} = (E_{corr} \mathbf{1} - m{D}) m{c}$,即 $m{c} = [E_{corr} \mathbf{1} - m{D}]^{-1} m{b}$,代回第一个方程,得 $E_{corr} = m{b}^\dagger m{c} = m{b}^\dagger [E_{corr} \mathbf{1} - m{D}]^{-1} m{b}$

练习4: 在CID方法中, 相关能最终的表达式为

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

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
$$|\Psi_0
angle=|1_1ar{1}_11_2ar{1}_2
angle$$
,以 $|\Psi_1
angle=|\Psi_{1_2ar{1}_2}^{2_2ar{2}_2}
angle=|1_1ar{1}_12_2ar{2}_2
angle$, $|\Psi_2
angle=|\Psi_{1_1ar{1}_1}^{2_1ar{2}_1}
angle=|2_1ar{2}_11_2ar{1}_2
angle$,试推导 $\langle\Psi_0|\hat{H}|\Psi_1
angle=\langle\Psi_0|\hat{H}|\Psi_2
angle=K_{12}$, $\langle\Psi_1|\hat{H}-E_0^{(\mathrm{HF})}|\Psi_1
angle=\langle\Psi_2|\hat{H}-E_0^{(\mathrm{HF})}|\Psi_2
angle=2\Delta$

解:

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:

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

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