Size-consistency problem in truncated CI calculations

EX5: Show that, for the dimer,

(i) the CID Hamiltonian matrix equals

$$\mathbf{H}^{\mathrm{CID}}(1+2) - E_{\mathrm{HF}}(1+2) = \begin{bmatrix} 0 & K & K \\ K & 2\Delta & 0 \\ K & 0 & 2\Delta \end{bmatrix}$$

(ii) the FCI Hamiltonian matrix equals

$$\mathbf{H}^{\mathrm{FCI}}(1+2) - E_{\mathrm{HF}}(1+2) = \begin{bmatrix} 0 & K & K & 0 \\ K & 2\Delta & 0 & K \\ K & 0 & 2\Delta & K \\ 0 & K & K & 4\Delta \end{bmatrix}$$

(iii) CID is not size-consistent since

$$E^{\mathrm{CID}}(1+2) = E_{\mathrm{HF}}(1+2) + \Delta - \sqrt{\Delta^2 + 2K^2} \neq E^{\mathrm{CID}}(1) + E^{\mathrm{CID}}(2)$$

(iv) FCI is size-consistent and $c_{12} = c^2$

H_2 dimer – minimal basis – Size consistency problem

(i) • The basis to be considered in CID is $\underbrace{|\Phi_0(1+2)\rangle}_{|HF\rangle}$, $\hat{D}_1|HF\rangle$ and $\hat{D}_2|HF\rangle$.

• $$H^{CID}(1+2) = \begin{bmatrix} E_{HF}(1+2) & \langle HF|\hat{H}\hat{D}_1|HF\rangle & \langle HF|\hat{H}\hat{D}_2|HF\rangle \\ \times & \langle \hat{D}_1 HF|\hat{H}\hat{D}_1|HF\rangle & \langle \hat{D}_1 HF|\hat{H}\hat{D}_2 HF\rangle \\ \times & \times & \langle \hat{D}_2 HF|\hat{H}\hat{D}_2|HF\rangle \end{bmatrix}$$

• $$\langle \hat{D}_1 HF|\hat{H}\hat{D}_1|HF\rangle = \underbrace{\langle \hat{D}_1 HF|\hat{H}_1\hat{D}_1|HF\rangle}_{2h_{uu} + \langle 1\sigma_u 1\sigma_u|1\sigma_u 1\sigma_u\rangle \to E_u} + \underbrace{\langle \hat{D}_1 HF|\hat{H}_2\hat{D}_1|HF\rangle}_{E_{HF}(2) \to E_g}$$

$$2h_{uu} + \langle 1\sigma_u 1\sigma_u|1\sigma_u 1\sigma_u\rangle = E_{HF}(1) + 2\Delta, \quad E_g \leftarrow E_{HF}(1)$$

where $2\Delta = 2(h_{uu} - h_{gg}) + \langle 1\sigma_u 1\sigma_u|1\sigma_u 1\sigma_u\rangle - \langle 1\sigma_g 1\sigma_g|1\sigma_g 1\sigma_g\rangle$
$= E_u - E_g$

• $$\langle \hat{D}_2 HF|\hat{H}\hat{D}_2|HF\rangle = \underbrace{\langle \hat{D}_2 HF|\hat{H}_1\hat{D}_2|HF\rangle}_{E_g} + \underbrace{\langle \hat{D}_2 HF|\hat{H}_2\hat{D}_2|HF\rangle}_{E_u}$$

$$= 2E_g + 2\Delta$$

• $$\langle HF|\hat{H}\hat{D}_2|HF\rangle = \underbrace{\langle HF|\hat{H}_1\hat{D}_2|HF\rangle}_{0} + \underbrace{\langle HF|\hat{H}_2\hat{D}_2|HF\rangle}_{K} = \langle HF|\hat{H}\hat{D}_1|HF\rangle$$

doesn't act on monomer 2.

• $$\langle \hat{D}_1 HF|\hat{H}\hat{D}_2|HF\rangle = 0$$

$$= \underbrace{\langle \hat{D}_1 HF|\hat{H}_1\hat{D}_2|HF\rangle}_{0} + \underbrace{\langle \hat{D}_1 HF|\hat{H}_2\hat{D}_2|HF\rangle}_{0}$$

does not act on monomer 2. does not act on monomer 1

Conclusion:

$$H^{CID}(1+2) = \begin{bmatrix} 2E_g & K & K \\ K & 2E_g+2\Delta & 0 \\ K & 0 & 2E_g+2\Delta \end{bmatrix}$$

or

$$H^{CID}(1+2) - 2E_g = \begin{bmatrix} 0 & K & K \\ K & 2\Delta & 0 \\ K & 0 & 2\Delta \end{bmatrix}$$

(ii) In FCI, the basis to be considered is the one of CID and $\hat{D}_1\hat{D}_2|HF\rangle$.

Therefore

$$H^{FCI}(1+2) = \begin{bmatrix} 2E_g & K & K & \langle HF|\hat{H}\hat{D}_1\hat{D}_2|HF\rangle \\ K & 2E_g+2\Delta & 0 & \langle \hat{D}_1 HF|\hat{H}\hat{D}_1\hat{D}_2|HF\rangle \\ K & 0 & 2E_g+2\Delta & \langle \hat{D}_2 HF|\hat{H}\hat{D}_1\hat{D}_2|HF\rangle \\ \times & \times & \times & \langle \hat{D}_1\hat{D}_2 HF|\hat{H}|\hat{D}_1\hat{D}_2|HF\rangle \end{bmatrix}$$

- $\langle HF|\hat{H}\hat{D}_1\hat{D}_2|HF\rangle = \underbrace{\langle HF|\hat{H}_1\hat{D}_1\hat{D}_2|HF\rangle}_{=0} + \underbrace{\langle HF|\hat{H}_2\hat{D}_1\hat{D}_2|HF\rangle}_{=0}$

  does not act on monomer 2.

  does not act on monomer 1.

- $\langle \hat{D}_1 HF|\hat{H}\hat{D}_1\hat{D}_2|HF\rangle = \underbrace{\langle \hat{D}_1 HF|\hat{H}_1\hat{D}_1\hat{D}_2|HF\rangle}_{=0} + \underbrace{\langle \hat{D}_1 HF|\hat{H}_2\hat{D}_1\hat{D}_2|HF\rangle}_{\to K}$

  does not act on monomer 2

  in this case, electrons on monomer 1 are in the state $|\sigma_u^2$ in the bra and the ket

- $\langle \hat{D}_2 HF|\hat{H}\hat{D}_1\hat{D}_2|HF\rangle = \underbrace{\langle \hat{D}_2 HF|\hat{H}_1\hat{D}_1\hat{D}_2|HF\rangle}_{\to K} + \underbrace{\langle \hat{D}_2 HF|\hat{H}_2\hat{D}_1\hat{D}_2|HF\rangle}_{\to 0}$

  in this case, electrons on monomer 2 are in the state $|\sigma_u^2$ in the bra and the ket.

  does not act on monomer 1.

- $\langle \hat{D}_1\hat{D}_2 HF|\hat{H}\,\hat{D}_1\hat{D}_2|HF\rangle = \underbrace{\langle \hat{D}_1\hat{D}_2 HF|\hat{H}_1\hat{D}_1\hat{D}_2|HF\rangle}_{\to E_u} + \underbrace{\langle \hat{D}_1\hat{D}_2 HF|\hat{H}_2\hat{D}_1\hat{D}_2|HF\rangle}_{\to E_u}$

  electrons on monomer 2 are in state $|\sigma_u^2$ in both bra and ket

  electrons on monomer 1 are in state $|\sigma_u^2$ in both bra and ket

Conclusion:

$$H^{FCI}(1+2) - 2E_g = \begin{bmatrix} 0 & K & K & 0 \\ K & 2\Delta & 0 & K \\ K & 0 & 2\Delta & K \\ 0 & K & K & 4\Delta \end{bmatrix}$$

(iii) Diagonalization of $H^{CID}(1+2) - 2E_g$:

$$\begin{vmatrix} -\lambda & k & k \\ k & 2\Delta-\lambda & 0 \\ k & 0 & 2\Delta-\lambda \end{vmatrix} = 0 \Leftrightarrow k \begin{vmatrix} k & 2\Delta-\lambda \\ k & 0 \end{vmatrix} + (2\Delta-\lambda) \begin{vmatrix} -\lambda & k \\ k & 2\Delta-\lambda \end{vmatrix}$$

$$\Leftrightarrow -k^2(2\Delta-\lambda) + (2\Delta-\lambda)\left[\lambda(\lambda-2\Delta) - k^2\right] = 0$$

$$\Leftrightarrow (2\Delta-\lambda)\left[\lambda^2 - 2\Delta\lambda - 2k^2\right] = 0$$

The eigenvalues are 2Δ, $\dfrac{2\Delta - \sqrt{4\Delta^2+8k^2}}{2}$, $\dfrac{2\Delta + \sqrt{4\Delta^2+8k^2}}{2}$

Conclusion: The CID ground-state energy for the dimer is $\boxed{2E_g + \Delta - \sqrt{\Delta^2+2k^2}}$

which should be compared to $E^{CID}(1) + E^{CID}(2)$.

For one monomer, the CID matrix equals $\begin{bmatrix} E_g & k \\ k & E_u \end{bmatrix} = E_g + \underbrace{\begin{bmatrix} 0 & k \\ k & 2\Delta \end{bmatrix}}$

eigenvalues are such that

$$\begin{vmatrix} -\lambda & k \\ k & 2\Delta-\lambda \end{vmatrix} = 0 \Leftrightarrow -\lambda(2\Delta-\lambda) - k^2 = 0$$

$$\Leftrightarrow \lambda^2 - 2\Delta\lambda - k^2 = 0$$

Therefore $E^{CID}(1) = E^{CID}(2) = E_g + \Delta - \sqrt{\Delta^2+k^2}$

$\rightarrow$ $\boxed{E^{CID}(1) + E^{CID}(2) = 2E_g + 2\Delta - 2\sqrt{\Delta^2+k^2} \neq E^{CID}(1+2)}$

(iv) Diagonalization of $H^{FCI}(1+2) - 2E_g$:

$$\begin{vmatrix} -\lambda & k & k & 0 \\ k & 2\Delta-\lambda & 0 & k \\ k & 0 & 2\Delta-\lambda & k \\ 0 & k & k & 4\Delta-\lambda \end{vmatrix} = 0 \Leftrightarrow k \begin{vmatrix} -\lambda & k & k \\ k & 0 & 2\Delta-\lambda \\ 0 & k & k \end{vmatrix} - k \begin{vmatrix} -\lambda & k & k \\ k & 2\Delta-\lambda & 0 \\ 0 & k & k \end{vmatrix} + (4\Delta-\lambda) \begin{vmatrix} -\lambda & k & k \\ k & 2\Delta-\lambda & 0 \\ k & 0 & 2\Delta-\lambda \end{vmatrix}$$

$$k\left[-\lambda\left(-k(2\Delta-\lambda)\right) - k\times 0\right] - k\left[-\lambda(2\Delta-\lambda)k\right] + (4\Delta-\lambda)\Big[k\left(-k(2\Delta-\lambda)\right) + (2\Delta-\lambda)\left(-\lambda(2\Delta-\lambda)-k^2\right)\Big] = 0$$

thus leading to

$$\lambda k^2(2\Delta-\lambda) + \lambda k^2(2\Delta-\lambda) + (4\Delta-\lambda)\left[-k^2(2\Delta-\lambda) - k^2(2\Delta-\lambda) - \lambda(2\Delta-\lambda)^2\right] = 0$$

$$\Leftrightarrow \quad 2\lambda k^2(2\Delta-\lambda) + (4\Delta-\lambda)\left[-2k^2(2\Delta-\lambda) - \lambda(2\Delta-\lambda)^2\right] = 0$$

$$\Leftrightarrow \quad -(2\Delta-\lambda)\Big[\lambda(4\Delta-\lambda)(2\Delta-\lambda) + \underbrace{2k^2(4\Delta-\lambda) - 2\lambda k^2}_{\downarrow \; 2k^2(4\Delta-2\lambda) = 4k^2(2\Delta-\lambda)}\Big] = 0$$

$$\Leftrightarrow \quad -(2\Delta-\lambda)^2\left[\lambda(4\Delta-\lambda) + 4k^2\right] = 0 \quad \Leftrightarrow \quad \lambda = 2\Delta \quad \text{or} \quad \lambda^2 - 4\Delta\lambda - 4k^2 = 0$$

$$\Updownarrow$$

$$\lambda = \frac{4\Delta \pm \sqrt{16\Delta^2 + 16k^2}}{2}$$

Conclusion: The FCI ground-state energy of the dimer equals

$$E^{FCI}(1+2) = 2E_g + 2\Delta - 2\sqrt{\Delta^2+k^2} = \underbrace{E^{FCI}(1)}_{E^{CID}(1)} + \underbrace{E^{FCI}(2)}_{E^{CID}(2)}$$

$\Rightarrow$ FCI is size-consistent.

- $|\Psi^{FCI}(1+2)\rangle = |HF\rangle + c_1 \hat{D}_1 |HF\rangle + c_2 \hat{D}_2 |HF\rangle + c_{12} \hat{D}_1 \hat{D}_2 |HF\rangle$

$$\Rightarrow \begin{bmatrix} 0 & k & k & 0 \\ k & 2\Delta & 0 & k \\ k & 0 & 2\Delta & k \\ 0 & k & k & 4\Delta \end{bmatrix} \begin{bmatrix} 1 \\ c_1 \\ c_2 \\ c_{12} \end{bmatrix} = 2\left(\Delta - \sqrt{\Delta^2 + k^2}\right) \begin{bmatrix} 1 \\ c_1 \\ c_2 \\ c_{12} \end{bmatrix}$$

$$\Rightarrow \begin{cases} kc_1 + kc_2 = 2\left(\Delta - \sqrt{\Delta^2+k^2}\right) & (1) \\ k + 2\Delta c_1 + kc_{12} = 2\left(\Delta - \sqrt{\Delta^2+k^2}\right) c_1 & (2) \\ k + 2\Delta c_2 + kc_{12} = 2\left(\Delta - \sqrt{\Delta^2+k^2}\right) c_2 & (3) \\ kc_1 + kc_2 + 4\Delta c_{12} = 2\left(\Delta - \sqrt{\Delta^2+k^2}\right) c_{12} & (4) \end{cases}$$

$(2)-(3) \Rightarrow 2\Delta(c_1 - c_2) = 2\left(\Delta - \sqrt{\Delta^2+k^2}\right)(c_1 - c_2)$

$\rightarrow -2\sqrt{\Delta^2+k^2}\,(c_1 - c_2) = 0 \Rightarrow \boxed{c_1 = c_2 = c}$

$(1) \Rightarrow \boxed{2kc = 2\left(\Delta - \sqrt{\Delta^2+k^2}\right)} \overset{(2)}{\Rightarrow} k + 2\Delta c + kc_{12} = 2kc^2 \quad (5)$

$\overset{(4)}{\Rightarrow} 2kc + 4\Delta c_{12} = 2kc\,c_{12} \quad (6)$

$2c \times (5) \Rightarrow 2kc + 4\Delta c^2 + 2kc_{12}c = 4kc^3 \quad (7)$

$(7)-(6) \Rightarrow 4\Delta(-c_{12} + c^2) + 2kc_{12}c = 4kc^3 - 2kc\,c_{12}$

$\Rightarrow 4\Delta(c^2 - c_{12}) = 4k(c^3 - c_{12}c) = 4kc(c^2 - c_{12})$

$\Rightarrow (\Delta - kc)(c^2 - c_{12}) = 0$

- Since $kc = \Delta - \sqrt{\Delta^2+k^2}$

$kc \neq \Delta$ otherwise $\Delta^2 = 0$ and $k^2 = 0$ (!)

therefore $\boxed{c_{12} = c^2}$

Conclusion:

$|\Psi^{FCI}(1+2)\rangle = |HF\rangle + c\hat{D}_1|HF\rangle + c\hat{D}_2|HF\rangle + c^2 \hat{D}_1 \hat{D}_2 |HF\rangle$

$= (1 + c\hat{D}_1 + c\hat{D}_2 + c^2 \hat{D}_1 \hat{D}_2)|HF\rangle$

$= \underbrace{e^{c\hat{D}_1 + c\hat{D}_2}|HF\rangle}_{\text{CC parameterization!}}$

Since

$e^{c\hat{D}_1 + c\hat{D}_2}|HF\rangle = \Big(1 + c\hat{D}_1 + c\hat{D}_2 + \frac{c^2(\hat{D}_1 + \hat{D}_2)^2}{2!}\Big)|HF\rangle + \underbrace{\sum_{n \geq 3} \frac{c^n(\hat{D}_1+\hat{D}_2)^n}{n!}|HF\rangle}_{\text{at least sextuple excitations!}} \rightarrow 0$

$= (1 + c\hat{D}_1 + c\hat{D}_2)|HF\rangle + \frac{c^2}{2}\hat{D}_1^2|HF\rangle + \frac{c^2}{2}\hat{D}_2^2|HF\rangle + \frac{c^2}{2}\hat{D}_1\hat{D}_2|HF\rangle + \frac{c^2}{2}\underbrace{\hat{D}_2\hat{D}_1}_{\hat{D}_1\hat{D}_2}|HF\rangle$

$\rightarrow 0$ (quadruple excitations on the monomer!)

Complements to the solution

$\boxed{C1}$ Simpler way to show that $c_{12} = c^2$:

- we have
$$\begin{cases} Kc_1 + Kc_2 = 2\left(\Delta - \sqrt{\Delta^2+K^2}\right) & (1) \\ K + 2\Delta c_1 + Kc_{12} = 2\left(\Delta - \sqrt{\Delta^2+K^2}\right)c_1 & (2) \\ K + 2\Delta c_2 + Kc_{12} = 2\left(\Delta - \sqrt{\Delta^2+K^2}\right)c_2 & (3) \end{cases}$$

(2) and (3) can be simplified as follows:

$$\begin{cases} K(1+c_{12}) = -2\sqrt{\Delta^2+K^2}\,c_1 & (2)' \\ K(1+c_{12}) = -2\sqrt{\Delta^2+K^2}\,c_2 & (3)' \end{cases} \Rightarrow \boxed{c_1 = c_2} \qquad (K \neq 0)$$

- If we "square" eq. (1) it comes $(2Kc)^2 = 4\left(\Delta - \sqrt{\Delta^2+K^2}\right)^2$

$$\Rightarrow K^2c^2 = \Delta^2 + (\Delta^2 + K^2) - 2\Delta\sqrt{\Delta^2+K^2}$$
$$= K^2 + 2\Delta\left(\Delta - \sqrt{\Delta^2+K^2}\right)$$

$$(4)' \quad \boxed{Kc^2 = K + 2\Delta c} \Leftarrow \boxed{K^2c^2 = K^2 + 2\Delta Kc}$$

- According to (2) we also have $Kc_{12} = \underbrace{2\left(\Delta - \sqrt{\Delta^2+K^2}\right)c}_{\overset{(1)}{=}\,2Kc} \underbrace{- K - 2\Delta c}_{(4)'}$

$$= 2Kc^2 - Kc^2$$
$$= Kc^2$$

$$\Rightarrow \boxed{c_{12} = c^2}$$

$\boxed{C_2}$ Coupled cluster wave function:

$$|FCI(1+2)\rangle = |HF\rangle + c(\hat{D}_1 + \hat{D}_2)|HF\rangle + c^2\hat{D}_1\hat{D}_2|HF\rangle$$
$$= (1 + c\hat{D}_1 + c\hat{D}_2 + c^2\hat{D}_1\hat{D}_2)|HF\rangle$$
$$= (1 + c\hat{D}_1)(1 + c\hat{D}_2)|HF\rangle$$

if we introduce the excitation operators $\hat{T}_1 = c\hat{D}_1$ and $\hat{T}_2 = c\hat{D}_2$

$$|FCI(1+2)\rangle = (1+\hat{T}_1)(1+\hat{T}_2)|HF\rangle = e^{\hat{T}_1}e^{\hat{T}_2}|HF\rangle \text{ since}$$

$$\hat{T}_1^2 = c^2\hat{D}_1^2 = c^2\hat{a}^\dagger_{u\alpha,1}\hat{a}^\dagger_{u\beta,1}\hat{a}_{g\beta,1}\hat{a}_{g\alpha,1}\hat{a}^\dagger_{u\alpha,1}\hat{a}^\dagger_{u\beta,1}\hat{a}_{g\beta,1}\hat{a}_{g\alpha,1}$$

$$\overset{\parallel}{0} \qquad = -c^2\hat{a}^\dagger_{u\alpha,1}\hat{a}^\dagger_{u\beta,1}\hat{a}_{g\beta,1}\hat{a}^\dagger_{u\alpha,1}\hat{a}^\dagger_{u\beta,1}\hat{a}_{g\beta,1}\hat{a}_{g\alpha,1}\hat{a}_{g\alpha,1} \quad \overset{\parallel}{0}$$

Similarly $\hat{T}_2^2 = 0 \Rightarrow e^{\hat{T}_2} = 1 + \hat{T}_2 + \underbrace{\frac{\hat{T}_2^2}{2!}}_{=0} + \underbrace{\frac{\hat{T}_2 \hat{T}_2^2}{3!}}_{=0} + \cdots$

(same for $e^{\hat{T}_1}$)

And since $[\hat{T}_1, \hat{T}_2] = 0$ it comes

$$\boxed{|FCI(1+2)\rangle = e^{\hat{T}_1 + \hat{T}_2} |HF\rangle \equiv |CCD\rangle}$$