CB2070 Ex session 10

① Hydrogen molecule, two electrons

We have

$$|\Psi_{HF}\rangle = |\sigma_g, \bar{\sigma}_g\rangle = |1, \bar{1}\rangle \quad \text{ground state}$$

$$|\Psi_{g\bar{g}}^{u\bar{u}}\rangle = |\sigma_u, \bar{\sigma}_u\rangle = |2, \bar{2}\rangle$$

where the bar denotes β-spin and no bar is α spin.

a) The CID wave function is

$$|\Psi_{CID}\rangle = c_0 |\Psi_{HF}\rangle + c_{g\bar{g}}^{u\bar{u}} |\Psi_{g\bar{g}}^{u\bar{u}}\rangle$$

and $E^{CID} = \langle \Psi_{CID} | \hat{H} | \Psi_{CID} \rangle$

from which we construct the CID matrix

$$H^{CID} = \begin{pmatrix} \langle \Psi_{HF} | \hat{H} | \Psi_{HF} \rangle & \langle \Psi_{HF} | \hat{H} | \Psi_{g\bar{g}}^{u\bar{u}} \rangle \\ \langle \Psi_{g\bar{g}}^{u\bar{u}} | \hat{H} | \Psi_{HF} \rangle & \langle \Psi_{g\bar{g}}^{u\bar{u}} | \hat{H} | \Psi_{g\bar{g}}^{u\bar{u}} \rangle \end{pmatrix}$$

$$= \begin{pmatrix} \langle 1\bar{1} | \hat{A} | 1\bar{1} \rangle & \langle 1\bar{1} | \hat{A} | 2\bar{2} \rangle \\ \langle 2\bar{2} | \hat{A} | 1\bar{1} \rangle & \langle 2\bar{2} | \hat{A} | 2\bar{2} \rangle \end{pmatrix}$$

b) We have $\hat{H} = \sum_i^N h(i) + \sum_{i,j>i}^N r_{ij}^{-1}$

From table 2.5 (p 72) we have the one- and two-electron operator matrix elements for a HF ground state and we get

1-elec $\langle 1\bar{1} | \hat{h} | 1\bar{1} \rangle = \langle 1 | \hat{h} | 1 \rangle + \langle \bar{1} | \hat{h} | \bar{1} \rangle = 2h_{11}$

$\langle 1\bar{1} | \hat{h} | 2\bar{2} \rangle = \langle 2\bar{2} | \hat{h} | 1\bar{1} \rangle = 0, \quad \langle 2\bar{2} | \hat{h} | 2\bar{2} \rangle = 2h_{22}$

$\langle 1 | \hat{h} | 1 \rangle = \langle \bar{1} | \hat{h} | \bar{1} \rangle$ comes when integrating over spin variables, such that only spatial orbitals are considered

2-elec $\langle 1\bar{1} | \hat{O}_2 | 1\bar{1} \rangle = \langle 1\bar{1} | 1\bar{1} \rangle - \langle 1\bar{1} | \bar{1}1 \rangle$ ← $= 0$ when integrating over spin

$= \langle 11 | 11 \rangle = (11|11)$ ← chemist's notation

$\langle 1\bar{1} | \hat{O}_2 | 2\bar{2} \rangle = \langle 1\bar{1} | 2\bar{2} \rangle - \langle 1\bar{1} | \bar{2}2 \rangle = \langle 11 | 22 \rangle = (12|12)$

$\langle 2\bar{2} | \hat{O}_2 | 1\bar{1} \rangle = \langle 2\bar{2} | 1\bar{1} \rangle - \langle 2\bar{2} | \bar{1}1 \rangle = \langle 22 | 11 \rangle = (21|21)$

$\langle 2\bar{2} | \hat{O}_2 | 2\bar{2} \rangle = \langle 2\bar{2} | 2\bar{2} \rangle - \langle 2\bar{2} | \bar{2}2 \rangle = (22|22)$

b) cont'd

$K_{12} = K_{21}$

Collecting the terms, we get

$$H^{CID} = \begin{pmatrix} 2h_{11} + (11|11) & (12|12) \\ (21|21) & 2h_{22} + (22|22) \end{pmatrix} = \begin{pmatrix} 2h_{11} + J_{11} & K_{12} \\ K_{21} & 2h_{22} + J_{22} \end{pmatrix}$$

with $E_{HF} = 2h_{11} + J_{11}$ in the first element

c) Inserting numerical values (in Python) we get

$$H^{CID} = \begin{pmatrix} -1.8308 & 0.1813 \\ 0.1813 & -0.2539 \end{pmatrix}$$

Solving the eigenvalue equation $H^{CID}C = C\varepsilon$ reveals

$E_{CID} = -1.8514$ a.u. (and $E_{HF} = -1.8308$ a.u.

$C_0 = -0.9936$

$C_{1\bar{1}}^{2\bar{2}} = -0.1128$

d) The CID estimate of the correlation energy is

$$E_{Corr}^{CID} = E_{CID} - E_{HF} = -0.02058 \text{ a.u.}$$

and in relative terms

$$\frac{E_{Corr}^{CID}}{E_{HF}} \cdot 100\% = 1.12\%$$

e) Calculating the percentage weight as

$$w_i = c_i^2 \cdot 100\%$$

we get

$w_0 = 98.73\%$

$w_{1\bar{1}}^{2\bar{2}} = 1.27\%$