

CB2070 Ex. session 12

① We partition the Hamiltonian as

$$\hat{H} = \hat{F} + \hat{V} + V^{n,\text{rep}}$$

with

$$\hat{F} = \sum_i^N \hat{f}(i) = \sum_i^N [\hat{h}(i) + \sum_j^N (\hat{j}_j(i) - \hat{K}_j(i))]$$

$$\begin{aligned} \hat{V} &= \hat{H} - \hat{F} = \sum_i^N \hat{h}(i) + \sum_{i>j}^N \hat{g}(i,j) - \sum_i^N \hat{h}(i) - \sum_{i,j}^N (\hat{j}_j(i) - \hat{K}_j(i)) \\ &= \sum_i^N \left[\sum_{j>i}^N \hat{g}(i,j) - \sum_j^N (\hat{j}_j(i) - \hat{K}_j(i)) \right] \end{aligned}$$

a) The unperturbed Hamiltonian is the Fock operator and we get $\Psi^{(0)}$ and $E^{(0)}$ from its lowest eigenvalue & corresponding eigenstate:

$$\begin{aligned} \hat{F}|\Phi_n\rangle &= \varepsilon_n |\Phi_n\rangle \\ \rightarrow \hat{F}|\Psi^{(0)}\rangle &= \varepsilon_0 |\Psi^{(0)}\rangle = F|\Psi^{HF}\rangle = \sum_i^N \varepsilon_i |\Psi^{HF}\rangle \end{aligned}$$

the HF wavefunction is an eigenfunction
of \hat{F}

where $\varepsilon_0 = \sum_i^N \varepsilon_i$ is the sum of energies of all occupied orbitals.

We determine the zeroth-order energy from

$$\begin{aligned} E^{(0)} &= \langle \Psi^{(0)} | \hat{F} | \Psi^{(0)} \rangle = \langle \Psi^{HF} | \hat{F} | \Psi^{HF} \rangle = \langle \bar{1}\bar{1} | \hat{F} | \bar{1}\bar{1} \rangle \\ &= \sum_{i=\bar{1},\bar{1}} \langle i | \hat{h} | i \rangle + \sum_{i=\bar{1},\bar{1}} \sum_{i=\bar{1},\bar{1}} \langle i | \hat{j}_j | i \rangle - \langle i | \hat{K}_j | i \rangle \\ &= h_{\bar{1}\bar{1}} + h_{\bar{1}\bar{1}} + \langle \bar{1}\bar{1} | \hat{g} | \bar{1}\bar{1} \rangle + \langle \bar{1}\bar{1} | \hat{g} | \bar{1}\bar{1} \rangle - \langle \bar{1}\bar{1} | \hat{g} | \bar{1}\bar{1} \rangle - \langle \bar{1}\bar{1} | \hat{g} | \bar{1}\bar{1} \rangle \\ &= 2h_{\bar{1}\bar{1}} + 2J_{\bar{1}\bar{1}} \\ &= -1.1562 \text{ a.u.} \end{aligned}$$

recall
 $\langle i | \hat{S}_z | i \rangle = \langle ij | \hat{g} | ij \rangle$
 $\langle i | \hat{R}_j | i \rangle = \langle ij | \hat{g} | ij \rangle$

This numerical result can also be obtained from our SCF calculation as $2 \times$ the first orbital energy (since the results are calculated for just one spin)

b) The first-order energy correction is

$$\begin{aligned} E^{(1)} &= \langle \Psi^{(0)} | \hat{V} | \Psi^{(0)} \rangle = \sum_{i=\bar{1},\bar{1}} \sum_{j>i} \langle ij | \hat{g} | ij \rangle - \langle ij | \hat{g} | ji \rangle - \sum_{i=\bar{1},\bar{1}} \sum_{j=\bar{1},\bar{1}} \langle ij | \hat{g} | ij \rangle - \langle ij | \hat{g} | ji \rangle \\ &= \frac{1}{2} \sum_{i,j=\bar{1},\bar{1}} \langle ij | \hat{g} | ij \rangle - \langle ij | \hat{g} | ji \rangle - \sum_{i,j=\bar{1},\bar{1}} \langle ij | \hat{g} | ij \rangle - \langle ij | \hat{g} | ji \rangle = -\frac{1}{2} \sum_{i,j=\bar{1},\bar{1}} \langle ij | \hat{g} | ij \rangle - \langle ij | \hat{g} | ji \rangle \\ &= -\frac{1}{2} (\langle \bar{1}\bar{1} | \hat{g} | \bar{1}\bar{1} \rangle - \langle \bar{1}\bar{1} | \hat{g} | \bar{1}\bar{1} \rangle + \langle \bar{1}\bar{1} | \hat{g} | \bar{1}\bar{1} \rangle - \langle \bar{1}\bar{1} | \hat{g} | \bar{1}\bar{1} \rangle) = -J_{\bar{1}\bar{1}} \end{aligned}$$

b) cont'd

The MP1 ground state energy becomes

$$E_{MP1} = E^{(0)} + E^{(1)} = 2h_{11} + 2J_{11} - J_{11} = 2h_{11} + J_{11} = E_{HF} \quad (= -1.8308 \text{ a.u.})$$

It is also possible to derive it "the other way around" by substituting \hat{V} with $\hat{H} - \hat{F}$ which will give an expression of the form $E_{HF} - E^{(0)}$

c) The other eigenstate of our zeroth order Hamiltonian (Fock operator) is, in our CIO-setup, the doubly excited determinant:

$$\hat{F}|\Psi_{gg}^{uu}\rangle = E_{gg}^{uu}|\Psi_{gg}^{uu}\rangle \quad \text{where the eigenvalue is the sum of the occupied orbital energies which is calculated as}$$

$$E_{gg}^{uu} = \underbrace{\epsilon_0}_{E^{(0)}} - \epsilon_g - \epsilon_{\bar{g}} + \epsilon_u + \epsilon_{\bar{u}}$$

The resolution-of-identity permutation operator becomes

$$\hat{P} = \sum_{M_2} |M_2\rangle \langle M_2| = |\Psi_{gg}^{uu}\rangle \langle \Psi_{gg}^{uu}| = |2\bar{2}\rangle \langle 2\bar{2}|$$

and the first-order correction to the wave function is determined

$$\begin{aligned} |\Psi^{(1)}\rangle &= -\hat{P}(\hat{F} - E^{(0)})^{-1} \hat{P} \hat{V} |\Psi^{(0)}\rangle \\ &= |\Psi_{gg}^{uu}\rangle \langle \Psi_{gg}^{uu}| (\hat{F} - E^{(0)})^{-1} |\Psi_{gg}^{uu}\rangle \langle \Psi_{gg}^{uu}| \hat{V} |\Psi^{HF}\rangle \end{aligned}$$

$\hookrightarrow \hat{F}$ working on the eigenstate $|\Psi_{gg}^{uu}\rangle$ is replaced by the eigenvalue $E^{(0)} - \epsilon_g - \epsilon_{\bar{g}} + \epsilon_u + \epsilon_{\bar{u}}$ such that

$$\langle \Psi_{gg}^{uu}| (E^{(0)} - \epsilon_g - \epsilon_{\bar{g}} + \epsilon_u + \epsilon_{\bar{u}} - E^{(0)}) |\Psi_{gg}^{uu}\rangle = \frac{\langle \Psi_{gg}^{uu} | \Psi_{gg}^{uu} \rangle}{\epsilon_u + \epsilon_{\bar{u}} - \epsilon_g - \epsilon_{\bar{g}}} = 1$$

For the matrix element with the HF ground state and a doubly excited determinant for one- and two-electron operators we have

$$\langle \Psi_{gg}^{uu} | \hat{h} | \Psi^{HF} \rangle = 0, \quad \langle \Psi_{gg}^{uu} | \hat{g} | \Psi^{HF} \rangle = \langle u\bar{u} | g\bar{g} \rangle - \langle u\bar{u} | g\bar{g} \rangle$$

So:

$$\begin{aligned} \langle \Psi_{gg}^{uu} | \hat{V} | \Psi^{HF} \rangle &= \langle \Psi_{gg}^{uu} | \hat{H} - \hat{F} | \Psi^{HF} \rangle = \langle \Psi_{gg}^{uu} | \hat{H} | \Psi^{HF} \rangle - \epsilon_0 \langle \Psi_{gg}^{uu} | \Psi^{HF} \rangle \\ &= \langle 2\bar{2} | 1\bar{1} \rangle - \langle 2\bar{2} | \bar{1}1 \rangle = \langle 2\bar{2} | 1\bar{1} \rangle = (12)(12) = K_{12} \end{aligned}$$

and thus

$$|\Psi^{(1)}\rangle = -|\Psi_{gg}^{uu}\rangle \frac{K_{12}}{\epsilon_2 + \epsilon_{\bar{2}} - \epsilon_1 - \epsilon_{\bar{1}}}$$

where $\epsilon_1 = \epsilon_1$, $\epsilon_2 = \epsilon_2$

c) cont'd

We can now determine the second-order correction to the energy:

$$\begin{aligned} E^{(2)} &= \langle \Psi^{(0)} | \hat{V} | \Psi^{(1)} \rangle = \langle \Psi^{\text{HF}} | \hat{H} | \Psi^{(1)} \rangle - \langle \Psi^{\text{HF}} | \hat{F} | \Psi^{(1)} \rangle \\ &= - \left\langle \Psi^{\text{HF}} | \hat{H} | \Psi_{g\bar{g}}^{u\bar{u}} \right\rangle \frac{K_{12}}{\epsilon_u + \epsilon_{\bar{u}} - \epsilon_g - \epsilon_{\bar{g}}} = - \frac{K_{12}^2}{\epsilon_u + \epsilon_{\bar{u}} - \epsilon_g - \epsilon_{\bar{g}}} \end{aligned}$$

with the numerical value $E^{(2)} = -0.0132 \text{ a.u.}$

The MP2 energy is then

$$E_{\text{MP2}} = E^{(0)} + E^{(1)} + E^{(2)} = E_{\text{HF}} + E^{(2)} = -1.844 \text{ a.u.}$$

d) To determine $\Psi^{(n+1)}$ and $E^{(n)}$ up to orders $n=6$, we recall the general expressions from RSPT

$$\Psi^{(m)} = -\hat{P}(\hat{H}_0 - E_0^{(n)})^{-1} \hat{P}[\hat{V}|\Psi^{(m-1)}\rangle - \sum_{k=1}^{m-1} E^{(k)} |\Psi^{(m-k)}\rangle]$$

$$E^{(m)} = \langle \Psi^{(m)} | \hat{V} | \Psi^{(m-1)} \rangle$$

We have $\hat{H}_0 = \hat{F}$, $\hat{P} = |\Psi_{g\bar{g}}^{u\bar{u}}\rangle \langle \Psi_{g\bar{g}}^{u\bar{u}}|$

Thus

$$\begin{aligned} \Psi^{(m)} &= - |\Psi_{g\bar{g}}^{u\bar{u}}\rangle \underbrace{\langle \Psi_{g\bar{g}}^{u\bar{u}} | (\hat{F} - E^{(m)})^{-1} | \Psi_{g\bar{g}}^{u\bar{u}} \rangle}_{\langle \Psi_{g\bar{g}}^{u\bar{u}} | \hat{V} | \Psi^{(m-1)} \rangle} - \sum_{k=1}^{m-1} E^{(k)} \langle \Psi_{g\bar{g}}^{u\bar{u}} | \Psi^{(m-k)} \rangle \\ &= (\epsilon_u + \epsilon_{\bar{u}} - \epsilon_g - \epsilon_{\bar{g}})^{-1} \end{aligned}$$

We already know

$$|\Psi^{(0)}\rangle = |\Psi^{\text{HF}}\rangle, E^{(0)} = E_0 = 2h_{11} + 2J_{11}, E^{(1)} = -\langle \eta/\eta \rangle = -J_{11}$$

$$|\Psi^{(1)}\rangle = - |\Psi_{g\bar{g}}^{u\bar{u}}\rangle \frac{\langle \bar{g}\bar{g} | \eta \rangle}{\epsilon_2 + \epsilon_{\bar{2}} - \epsilon_g - \epsilon_{\bar{g}}} = - |\Psi_{g\bar{g}}^{u\bar{u}}\rangle \frac{K_{12}}{2(\epsilon_2 - \epsilon_1)} \quad \begin{aligned} \epsilon_2 &= \epsilon_u \\ \epsilon_1 &= \epsilon_g \end{aligned}$$

$$\begin{aligned} |\Psi^{(2)}\rangle &= - |\Psi_{g\bar{g}}^{u\bar{u}}\rangle \frac{1}{2(\epsilon_u - \epsilon_g)} \left[\frac{-K_{12}}{2(\epsilon_u - \epsilon_g)} \langle \Psi_{g\bar{g}}^{u\bar{u}} | \hat{V} | \Psi_{g\bar{g}}^{u\bar{u}} \rangle \right. \\ &\quad \left. - (-J_{11}) \frac{-K_{12}}{2(\epsilon_u - \epsilon_g)} \underbrace{\langle \Psi_{g\bar{g}}^{u\bar{u}} | \Psi_{g\bar{g}}^{u\bar{u}} \rangle}_{=1} \right] \end{aligned}$$

We notice that for every m , only $|\Psi_{g\bar{g}}^{u\bar{u}}\rangle$ is involved and that the integrals will be identical. The difference for each m is multiplication by $(2(\epsilon_u - \epsilon_g))^{-1}$ and the prefactor of wavefunction correction $m-1$.

Q) cont'd

We evaluate

$$\begin{aligned}\langle \Psi_{g\bar{g}}^{uu} | \hat{V} | \Psi_{g\bar{g}}^{uu} \rangle &= \langle \Psi_{g\bar{g}}^{uu} | \hat{H} | \Psi_{g\bar{g}}^{uu} \rangle - \langle \Psi_{g\bar{g}}^{uu} | \hat{F} | \Psi_{g\bar{g}}^{uu} \rangle \\ &= \sum_{i=2, \bar{2}} \langle i | h | i \rangle + \sum_{i=2, \bar{2}} \sum_{j \neq i} \langle ij | ij \rangle - \langle ij | ji \rangle - E^{(e)} - \varepsilon_g - \varepsilon_{\bar{g}} + \varepsilon_a + \varepsilon_{\bar{a}} \\ &= h_{22} + h_{\bar{2}\bar{2}} + \langle 2\bar{2} | 2\bar{2} \rangle - \langle \bar{2}\bar{2} | 2\bar{2} \rangle = 2h_{11} - 2J_{11} - 2(\varepsilon_2 - \varepsilon_1)\end{aligned}$$

Collecting the terms

$$|\Psi^{(e)}\rangle = |\Psi_{g\bar{g}}^{uu}\rangle \frac{K_{12}}{4(\varepsilon_a - \varepsilon_g)^2} \underbrace{(2h_{22} + J_{22} - 2h_{11} - 2J_{11} - 2(\varepsilon_2 - \varepsilon_1) + J_{11})}_{E^{(e)}}$$

This can be greatly simplified by realizing that

$$\varepsilon_1 = h_{11} + J_{11}, \quad \varepsilon_2 = h_{22} + J_{22}$$

$$\begin{aligned}\rightarrow 2h_{22} + J_{22} - 2(h_{22} + J_{22}) - (2h_{11} + 2J_{11}) + 2(h_{11} + J_{11}) + J_{11} \\ = J_{11} - J_{22}\end{aligned}$$

And we get

$$|\Psi^{(e)}\rangle = |\Psi_{g\bar{g}}^{uu}\rangle \frac{K_{12}(J_{11} - J_{22})}{[2(\varepsilon_2 - \varepsilon_1)]^2}$$

② With the standard expression for the MP2 energy

$$E_{MP2} = - \sum_{i,j,s,t} \frac{(i|s)(j|t)[2(s|i|t) - (s|t)i|t)]}{\epsilon_s + \epsilon_t - \epsilon_i - \epsilon_j}$$

and $i,j = 1, s,t = 2$

we get for our H_2 setup

$$E_{MP2} = - \frac{(12|12)[2(21|21) - (21|21)21]}{\epsilon_2 + \epsilon_2 - \epsilon_1 - \epsilon_1} = \frac{(12|12)(21|21)}{2(\epsilon_2 - \epsilon_1)} = \frac{k_{12}^2}{2(\epsilon_2 - \epsilon_1)}$$

which is exactly the result from exercise 1.c in problem session 12