CB2070 Ex. session 11

(1) We write the CID ground state wave function in the form

$$|\Psi(\theta)\rangle = \cos\theta\,|\Psi_{HF}\rangle + \sin\theta\,|\Psi_{g\bar{g}}^{u\bar{u}}\rangle$$

a) The energy is

$$E(\theta) = \langle\Psi(\theta)|\hat{H}|\Psi(\theta)\rangle$$

$$= \left[\cos\theta\langle\Psi_{HF}| + \sin\theta\langle\Psi_{g\bar{g}}^{u\bar{u}}|\right]\hat{H}\left[\cos\theta|\Psi_{HF}\rangle + \sin\theta|\Psi_{g\bar{g}}^{u\bar{u}}\rangle\right]$$

$$= \cos^2\theta\langle\Psi_{HF}|\hat{H}|\Psi_{HF}\rangle + \sin^2\theta\langle\Psi_{g\bar{g}}^{u\bar{u}}|\hat{H}|\Psi_{g\bar{g}}^{u\bar{u}}\rangle$$
$$+ \cos\theta\sin\theta\langle\Psi_{HF}|\hat{H}|\Psi_{g\bar{g}}^{u\bar{u}}\rangle + \sin\theta\cos\theta\langle\Psi_{g\bar{g}}^{u\bar{u}}|\hat{H}|\Psi_{HF}\rangle$$

From prob. session 10, ex. 1.b we have that

$$\langle\Psi_{HF}|\hat{H}|\Psi_{g\bar{g}}^{u\bar{u}}\rangle = \langle\Psi_{g\bar{g}}^{u\bar{u}}|\hat{H}|\Psi_{HF}\rangle = (12|12)$$

so we get:

$$E(\theta) = \cos^2\theta E_{HF} + \sin^2\theta E_{u\bar{u}} + (\cos\theta\sin\theta + \sin\theta\cos\theta)(12|12)$$
$$= \cos^2\theta E_{HF} + \sin^2 E_{u\bar{u}} + \sin 2\theta\,(12|12)$$

where we have used the sine "angle sum identity":

$$\sin(\alpha+\beta) = \sin\alpha\cos\beta + \cos\alpha\sin\beta$$

with $\alpha=\beta=\theta$ we have $\cos\theta\sin\theta + \sin\theta\cos\theta = \sin 2\theta$

b) We minimize the energy by $\frac{dE(\theta)}{d\theta} = 0$

$$\frac{dE(\theta)}{d\theta} = \underbrace{\frac{d}{d\theta}\cos^2\theta}_{A} E_{HF} + \underbrace{\frac{d}{d\theta}\sin^2\theta}_{B} E_{u\bar{u}} + \underbrace{\frac{d}{d\theta}\sin 2\theta}_{C}\,(12|12)$$

Differentiating the terms separately (for clarity)

$$A: \frac{d}{d\theta}\cos^2\theta = \frac{d\cos\theta}{d\theta}\cos\theta + \cos\theta\frac{d\cos\theta}{d\theta} = -\sin\theta\cos\theta - \cos\theta\sin\theta$$
$$= -(\sin\theta\cos\theta + \cos\theta\sin\theta) = -\sin 2\theta$$

$$B: \frac{d}{d\theta}\sin^2\theta = \frac{d\sin\theta}{d\theta}\sin\theta + \sin\theta\frac{d\sin\theta}{d\theta} = \cos\theta\sin\theta + \sin\theta\cos\theta = \sin 2\theta$$

$$C: \frac{d}{d\theta}\sin 2\theta = \frac{d\sin 2\theta}{d\theta}\,\frac{d2\theta}{d\theta} = 2\cos 2\theta$$

b) cont'd

We insert the trigonometric derivatives

$$\frac{dE(\theta)}{d\theta} = -\sin 2\theta\, E_{HF} + \sin 2\theta\, E_{u\bar{u}} + 2\cos 2\theta\,(12|12)$$

$$= -\sin 2\theta\,(E_{HF} - E_{u\bar{u}}) + 2\cos 2\theta\,(12|12) = 0$$

$$\Rightarrow -\sin 2\theta\,(E_{HF} - E_{u\bar{u}}) = -2\cos 2\theta\,(12|12)$$

$$\Rightarrow \quad \sin 2\theta = 2\cos 2\theta\,\frac{(12|12)}{E_{HF} - E_{u\bar{u}}}$$

$$\Rightarrow \frac{\sin 2\theta}{\cos 2\theta} = 2\,\frac{(12|12)}{E_{HF} - E_{u\bar{u}}} = \tan 2\theta$$

we use $\arctan(\tan(2\theta)) = 2\theta$

$$2\theta = \arctan\left[\frac{2(12|12)}{E_{HF} - E_{u\bar{u}}}\right]$$

Multiplying by $\frac{1}{2}$ we have thus shown that the energy is minimized by

$$\theta = \frac{1}{2}\arctan\left[\frac{2(12|12)}{E_{HF} - E_{u\bar{u}}}\right]$$

c) In a Jupyter notebook we compute

$E_{u\bar{u}} = 2h_{22} + J_{22}$, $E_{HF} = 2h_{11} + J_{11}$, θ according to the eq above

and $E(\theta)$ according to the eq. in ex 1.b

We get the same result as for CID in problem session 10
$E^{CID} = -1.8514$ a.u.

② For RSPT we partition the Hamiltonian

$\hat{H} = \hat{H}_0 + \hat{V} + \hat{V}^{nrep}$ we don't care about this nuclear part

$\hat{H}_0$ has the orthonormal eigenstates which form the basis for our RSPT wave function

$$\hat{H}_0|\Phi_n\rangle = \mathcal{E}_n|\Phi_n\rangle$$

a) We determine $\Psi^{(0)}$ and $E^{(0)}$ from the zeroth-order equation

$$(\hat{H}_0 - E^{(0)})|\Psi^{(0)}\rangle = 0 \;\Rightarrow\; \hat{H}_0|\Psi^{(0)}\rangle = E^{(0)}|\Psi^{(0)}\rangle$$

$\Rightarrow \Psi^{(0)}$ and $E^{(0)}$ are the lowest eigenvalue/state in the basis:

$|\Psi^{(0)}\rangle = |\Phi_0\rangle$, $E^{(0)} = \mathcal{E}_0$

a) cont'd

In a Jupyter notebook we determine $E^{(0)}, \Psi^{(0)}$ by diagonalizing

$$H_0 = \begin{pmatrix} 2h_{11} & 0 \\ 0 & 2h_{22} \end{pmatrix}$$

and we get the zeroth-order energy and wf as the lowest eigenvalue and the corresponding eigenstate

$$E^{(0)} = \mathcal{E}_0 = 2h_{11} = -2.5054 \text{ a.u.}, \quad |\Psi^{(0)}\rangle = |\Phi_0\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

the second eigenvalue and -state are

$$\mathcal{E}_1 = 2h_{22} = -0.9514, \quad |\Phi_1\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

b) The first-order correction to the energy is

$$E^{(1)} = \langle \Psi^{(0)} | \hat{V} | \Psi^{(0)} \rangle$$

We have

$$\hat{V} = \begin{pmatrix} (11|11) & (12|12) \\ (12|12) & (22|22) \end{pmatrix}$$

and thus

$$E^{(1)} = \begin{pmatrix} 1 & 0 \end{pmatrix} \begin{pmatrix} (11|11) & (12|12) \\ (12|12) & (22|22) \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = (11|11) = 0.6746 \text{ a.u.}$$

The first-order RSPT energy becomes

$$E^{RSPT1} = E^{(0)} + E^{(1)} = -1.8308$$

which is exactly E_{HF}

c) Writing the first-order wave function correction

$$|\Psi^{(1)}\rangle = -(H_0 - E^{(0)})^{-1} \hat{V} |\Psi^{(0)}\rangle = -\begin{pmatrix} 2h_{11}-2h_{11} & 0 \\ 0 & 2h_{22}-2h_{11} \end{pmatrix}^{-1} \begin{pmatrix} (11|11) & (12|12) \\ (12|12) & (22|22) \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

if we accept that we can take the inverse of a matrix with a zero in the diagonal, we get

$$|\Psi^{(1)}\rangle = -\begin{pmatrix} 0 & 0 \\ 0 & \frac{1}{2h_{22}-2h_{11}} \end{pmatrix} \begin{pmatrix} (11|11) & (12|12) \\ (12|12) & (22|22) \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = -\frac{\overbrace{(12|12)}^{=K_{12}}}{2h_{22}-2h_{11}} \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

which is $c_1^{(1)} \Phi_1$ where $c_1^{(1)}$ is an expansion coefficient for the other eigenstate of the zeroth-order Hamiltonian, see MQM book p 324

c) cont'd

The second-order correction to the energy becomes

$$E^{(2)} = \langle \Psi^{(0)} | \hat{V} | \Psi^{(1)} \rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \begin{pmatrix} (11|11) & (12|12) \\ (12|12) & (22|22) \end{pmatrix} \left(-\frac{(12|12)}{2h_{22}-2h_{11}} \right) \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$= -\frac{K_{12}^2}{2h_{22}-2h_{11}} \qquad \text{where } K_{12} = (12|12)$$

Inserting numerical values, we get

$$|\Psi^{(1)}\rangle = -0.1167 \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \quad E^{(2)} = -0.02115 \text{ a.u.}$$

and the second-order RSPT energy becomes

$$E^{RSPT2} = E^{(0)} + E^{(1)} + E^{(2)} = -1.8520 \text{ a.u.}$$

d) The RSPT wavefunction to first order is

$$|\Psi^{PT1}\rangle = |\Phi_0\rangle + c_1^{(1)} |\Phi_1\rangle = |\Psi_{HF}\rangle + c_1^{(1)} |\Psi_{g\bar{g}}^{u\bar{u}}\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} - 0.1167 \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

The PT wave function is not normalized by construction so we normalize by

$$N = \langle \Psi^{PT1} | \Psi^{PT1} \rangle^{-\frac{1}{2}}$$

and we get the coefficients

$$|\Psi^{PT1}\rangle = c_0^{(0)} |\Psi_{HF}\rangle + c_1^{(1)} |\Psi_{g\bar{g}}^{u\bar{u}}\rangle = 0.993 \begin{pmatrix} 1 \\ 0 \end{pmatrix} - 0.116 \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

and the weights

$$(c_0^{(0)})^2 = 0.987, \quad (c_1^{(1)})^2 = 0.013$$
$$(98.7\%) \qquad (1.3\%)$$

The results agree with our assumption that the perturbation is rather small compared to the zeroth-order approximation.