FYS4480/9480, lecture
November 20, 2025

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FCI

$$\mathcal{H}|\Psi_0\rangle = E_0|\Psi_0\rangle$$

$$|\Psi_0\rangle = (1+\hat{C})|\Phi_0\rangle$$

$$\mathcal{H}_0|\Phi_0\rangle = \varepsilon_0|\Phi_0\rangle$$

$$\Delta E_0 = E_0 - E_0^{Ref}$$

$$E_0^{Ref} = \langle\Phi_0|\mathcal{H}|\Phi_0\rangle$$

$$\hat{C} = \sum_{PH>0} C_H^P \hat{A}_H^P |\Phi_0\rangle$$

$$\hat{A}_H^P = a_a^\dagger a_b^\dagger \cdots a_j \cdots a_j a_i$$

$$|\Psi_0\rangle = \exp\{\hat{T}\}\,|\Phi_0\rangle$$

$$\hat{T} = \underset{\text{1p1h}}{\hat{T}_1} + \underset{\text{2p2h}}{\hat{T}_2} - \cdots T_{\text{NP.NH}}$$

$$\underset{\text{1p1h}}{\hat{T}_1} = \sum_{ai} a_a^\dagger a_i\, t_i^a$$

↑ unknown amplitudes

$$\underset{\text{2p2h}}{\hat{T}_2} = \frac{1}{4} \sum_{\substack{ab\\ij}} t_{ij}^{ab} \underbrace{(a_a^\dagger a_i)(a_b^\dagger a_j)}_{a_a^\dagger a_b^\dagger a_j a_i}$$

$$|\Psi_0\rangle = e^{T}|\Phi_0\rangle$$

$$\mathcal{H} e^{T}|\Phi_0\rangle = E_0 e^{T}|\Phi_0\rangle$$

$$e^{-T}\mathcal{H}e^{T}|\Phi_0\rangle = E_0|\Phi_0\rangle$$

$$\mathcal{H} = \mathcal{H}_N + E_0^{\mathrm{ref}}$$

$$\underbrace{e^{-T}\mathcal{H}_N e^{T}}|\Phi_0\rangle = \Delta E_0 |\Phi_0\rangle$$

$$\mathcal{H}_N = \underbrace{\hat{F}_N}_{\text{onebody}} + \underbrace{\hat{V}_N}_{\text{twobody}}$$

Look back at FCI:

$$\mathcal{H}|\Psi_0\rangle = E_0|\Psi_0\rangle$$

$$\mathcal{H}\sum_{PH} c_H^P |\Phi_H^P\rangle \qquad \left\{ |\Phi_H^P\rangle = A_H^P |\Phi_0\rangle \right.$$

$$\langle\Phi_0|\mathcal{H}|\Phi_H^P\rangle \qquad = E_0 \sum_{PH} c_H^P |\Phi_H^P\rangle$$

$$\begin{bmatrix} \mathcal{H}_{00} & \mathcal{H}_{01} & \cdots & \mathcal{H}_{0NPNH} \\ \mathcal{H}_{01} & & & \\ \vdots & & & \\ \mathcal{H}_{0NPNH} & & & \mathcal{H}_{NPNH\,NPNH} \end{bmatrix} \begin{bmatrix} c_0 \\ c_1 \\ \vdots \\ \vdots \end{bmatrix}$$

$$\langle \Phi_0 | \mathcal{H} \sum_{PH} c_H^P | \Phi_H^P \rangle = \langle \Phi_0 | E_0 | \sum_{PH} c_H^P \times | \Phi_H^P \rangle$$

$$c_0 = 1$$

$$\langle \Phi_0 | \mathcal{H} | \Phi_0 \rangle + \sum_{ai} c_i^a \langle \Phi_0 | \mathcal{H} | \Phi_i^a \rangle$$

$$+ \sum_{\substack{ab \\ ij}} c_{ij}^{ab} \langle \Phi_0 | \mathcal{H} | \Phi_{ij}^{ab} \rangle = E_0$$

$$E_0^{\mathrm{ReF}} + \sum_{ai} c_i^a \langle i | f | a \rangle$$

$$+ \sum_{\substack{ab \\ ij}} c_{ij}^{ab} \langle ab | v | ij \rangle_{AS} = E_0$$

$$\Delta E_0 = E_0 - E_0^{Ref} =$$

$$\sum_{ai} c_i^a \langle i|f|a\rangle + \sum_{\substack{ij \\ ab}} c_{ij}^{ab} \langle ab||ij\rangle$$

$$\langle \Phi_i^a | H \sum_{PH} c_H^P | \Phi_H^P \rangle$$

$$= \langle \Phi_i^a | E_0 | \sum_{PH} c_H^P | \Phi_H^P \rangle$$

$$= E_0 \, c_i^a$$

$$= \langle \Phi_i^a | \mathcal{H} | \Phi_0 \rangle$$

$$+ \sum_{bj} c_j^b \langle \Phi_i^a | \mathcal{H} | \Phi_j^b \rangle$$

$$+ \sum_{\substack{bc \\ jk}} c_{jk}^{bc} \langle \Phi_i^a | \mathcal{H} | \Phi_{jk}^{bc} \rangle$$

$$+ \sum_{\substack{bcd \\ jke}} c_{jke}^{bcd} \langle \Phi_i^a | \mathcal{H} | \Phi_{jke}^{bcd} \rangle$$

$$\langle \Phi_{ij}^{ab} | \mathcal{H} \sum_{PH} C_H^P | \Phi_H^P \rangle = E_0 C_{ij}^{ab}$$

$$\langle ae \| u \| ij \rangle$$

$$\langle \Phi_{ij}^{ab} | \mathcal{H} | \Phi_0 \rangle + \sum_{ck} C_k^c \langle \Phi_{ij}^{ab} | \mathcal{H}$$

$$\times | \Phi_k^c \rangle + \sum_{\substack{cd \\ kl}} C_{kl}^{cd} \langle \Phi_{ij}^{ab} | \mathcal{H} | \Phi_{kl}^{cd} \rangle$$

$$+ \sum_{\substack{cde \\ klm}} C_{klm}^{cde} \langle \Phi_{ij}^{ab} | \mathcal{H} | \Phi_{klm}^{cde} \rangle$$

$$+ \sum_{\substack{cdef \\ klmn}} C_{klmn}^{cdef} \langle - - - \rangle$$

CC theory

approx : $T = T_2 = \frac{1}{4} \sum_{\substack{ab \\ ij}} t_{ij}^{ab} \, a_a^{\dagger} a_b^{\dagger} a_j a_i$

[CCD, D = double = 2p2h]

$$e^{T} |\Phi_0\rangle \simeq e^{T_2} |\Phi_0\rangle$$

$T_1 = 0$ all $t_i^a = 0$

$$H e^{T_2} |\Phi_0\rangle = E_{CCD}\, e^{T_2} |\Phi_0\rangle$$

$\langle \Phi_0 |$ and $\langle \Phi_{ij}^{ab} |$

$$e^{T_2} = \left(1 + T_2 + \frac{1}{2!} T_2^2 + \cdots\right)$$

$$\langle \Phi_0 | H e^{T_2} | \Phi_0 \rangle = E_{CCD} \langle \Phi_0 | e^{T_2} | \Phi_0 \rangle$$

$$= E_0$$

$$\langle \Phi_0 | H \left(1 + T_2 + \frac{1}{2!} T_2^2 \cdots\right) | \Phi_0 \rangle$$

$$\underbrace{\langle \Phi_0 | H | \Phi_0 \rangle}_{E_{Ref}} + \langle \Phi_0 | H T_2 | \Phi_0 \rangle = E_{CCD}$$

$T_2^2 | \Phi_0 \rangle \propto$ 4p4h state.

$$\langle \Phi_c | \mathcal{H} T_2 | \Phi_0 \rangle = \Delta E_{CCD} = E_{CCD} - E_0^{ref}$$

$$\mathcal{H} = E_0^{ref} + \hat{F}_N + \hat{V}_N$$

$$\langle \Phi_c | T_2 | \Phi_0 \rangle E_0^{ref} + \langle \Phi_c | \hat{F}_N T_2 | \Phi_0 \rangle$$

$$a_p^\dagger a_q \qquad a_a^\dagger a_b^\dagger a_j a_i$$

$$+ \langle \Phi_c | V_N T_2 | \Phi_0 \rangle$$

$$\langle \Phi_c | a_p^\dagger a_q \, a_a^\dagger a_b^\dagger a_j a_i | \Phi_0 \rangle$$

$$\langle \Phi_0 | V_N T_2 | \Phi_0 \rangle = \Delta E_{CCD}$$

$$= \left(\frac{1}{4}\right)^2 \sum_{\substack{pqrs\\ abij}} \langle \Phi_0 | a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_b^\dagger a_j a_i | \Phi_0 \rangle$$

δ_{sb} δ_{ra} δ_{qj} δ_{pi}

$$\times \langle pq | v | rs \rangle t_{ij}^{ab}$$

$$= \frac{1}{4} \sum_{\substack{ab\\ ij}} t_{ij}^{ab} \langle ij | v | ab \rangle = \Delta E_{CCD}$$

$= 0$ with HF

FCI: $\Delta E_0 = \sum_{ai} C_i^a \langle i | f | a \rangle + \sum_{\substack{ab\\ ij}} C_{ij}^{ab} \langle ij | v | ab \rangle$

$$\langle \Phi_{ij}^{ab} | H e^{T_2} | \Phi_0 \rangle =$$

$$\langle \Phi_{ij}^{ab} | E_0 \left(1 + T_2 + \frac{T_2^2}{2!} + \dots \right) | \Phi_0 \rangle$$

$$= \langle \Phi_{ij}^{ab} | T_2 | \Phi_0 \rangle E_0$$

$$= \langle \Phi_0 | a_i^\dagger a_j^\dagger a_b a_a \frac{1}{4} \sum_{\substack{cd \\ kl}} t_{kl}^{cd}$$

$$a_c^\dagger a_d^\dagger a_l a_k | \Phi_0 \rangle \times$$

$$E_0$$

$$a_i^\dagger a_j^\dagger a_b a_a a_c^\dagger a_d^\dagger a_e a_k$$

4 terms

$$t_{ij}^{ab} = -t_{ji}^{ab} = -t_{ij}^{ba} = t_{ji}^{ba}$$

$$= E_0 t_{ij}^{ab}$$

$$= \langle \Phi_{ij}^{ab} | H e^{T_2} | \Phi_0 \rangle$$

$$= \langle \Phi_{ij}^{ab} | (E_0^{ref} + F_N + V_N)\left(1 + T_2 + \frac{T_2^2}{2} + \dots\right) | \Phi_0 \rangle$$

$$\langle \Phi_{ij}^{ab} | (F_N + V_N)(1 + T_2 + \tfrac{1}{2} T_2^2 + \cdots) | \Phi_0 \rangle$$

$$= (E_{CCD} - E_0^{ref})\, t_{ij}^{ab} =$$

$$\Delta E_{CCD}\, t_{ij}^{ab}$$

$$\downarrow$$

$$\frac{1}{4} \sum_{\substack{cd\\kl}} t_{kl}^{cd} \langle kl | v | cd \rangle$$

non-linear in t_{ij}^{ab}

(unknown)

$$\langle \Phi_{ij}^{ab} | (F_N + V_N)(1 + T_2 + \tfrac{1}{2} T_2^2 + \cdots) | \Phi_0 \rangle$$

(i) $\langle \Phi_{ij}^{ab} | F_N | \Phi_0 \rangle = 0$

(ii) $\langle \Phi_{ij}^{ab} | F_N T_2 | \Phi_0 \rangle = ?$

(iii) $\langle \Phi_{ij}^{ab} | F_N T_2^2 | \Phi_0 \rangle = 0$

(iv) $\langle \Phi_{ij}^{ab} | V_N | \Phi_0 \rangle \neq 0$

(v) $\langle \Phi_{ij}^{ab} | V_N T_2 | \Phi_0 \rangle \neq 0$

(vi) $\langle \Phi_{ij}^{ab} | V_N T_2^2 | \Phi_0 \rangle \neq 0$

$$F_N = \sum_{pq} \langle p|f|q\rangle \, a_p^{+} a_q$$

$$\sum_{\substack{pq\\ cd\\ ek}} \underbrace{\langle \Phi_{ij}^{af} | a_p^{+} a_q \; a_c^{+} a_d^{+} a_e a_k | \Phi_0 \rangle} \times t_{ke}^{cd} \langle p|f|q\rangle \cdot \frac{1}{4}$$

$$\langle \Phi_0 | a_i^{+} a_j^{+} a_f a_a \; a_p^{+} a_q \; a_c^{+} a_d^{+} a_e a_k | \Phi_0 \rangle$$

$$\delta_{ik} \, \delta_{je} \, \delta_{fd} \, \delta_{ap} \, \delta_{qc}$$

$$\frac{1}{4} \sum_{c} \langle a|f|c\rangle \, t_{ij}^{cf}$$

$$a_i^+ a_j^+ a_b a_a \; a_p^+ a_q \; a_c^+ a_d^+ a_e a_k$$

$$- \sum_e \langle e | f | j \rangle \, t_{ie}^{ab}$$

two more terms

$$- \sum_k \langle k | f | i \rangle \, t_{kj}^{ab}$$

$$+ \sum_d \langle b | f | d \rangle \, t_{ij}^{ad}$$