FYS4480/9480, lecture
November 14, 2025

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FCI

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

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

$$= \sum_{PH>0} C_H^P \underbrace{A_H^P}_{} |\Phi_c\rangle$$

example

$$\sum_{ai} C_i^a \, a_a^\dagger a_i |\Phi_c\rangle$$

$$|\Psi_0\rangle_{(\mathrm{MBPT(RS)})} = \sum_{k=0}^{\infty} \left\{ \left[\hat{R}\hat{H}_I \right]^k |\Phi_0\rangle \right\}_L$$

$$\hat{R} = \sum_{M>0} \frac{|\Phi_M\rangle\langle\Phi_M|}{E_0 - E_M}$$

CC-Theory

$$\hat{T} = \underbrace{\hat{T}_1}_{1p1h} + \underbrace{\hat{T}_2}_{2p2h} + \dots + \hat{T}_{NpNh}$$

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

$$T = T_1 = \sum_{ai} t_i^a a_a^+ a_i$$

$$= \sum_{ai} t_i^a a_a^+ a_i$$

$$|\Psi_0\rangle = \exp\{T_1\}|\Phi_0\rangle$$

$$= \exp\left\{\sum_{ai} t_i^a a_a^+ a_i\right\}|\Phi_0\rangle$$

$$= \prod_{i \leq F}\left\{1 + \sum_{a>F} t_i^a a_a^+ a_i + \frac{1}{2!}\left(\sum_a t_i^a a_a^+ a_i\right)^2 + \cdots\right\}|\Phi_0\rangle$$

$$\cdots a_i a_i \cdots |\Phi_0\rangle$$

$$|\Psi_0\rangle = \prod_{i\in F}\left(1+\sum_a t_i^a a_a^\dagger a_i\right)|\Phi_0\rangle$$

T_2 : 2p2h

$$a_a^\dagger a_b^\dagger a_j a_i |\Phi_0\rangle = |\Phi_{ij}^{ab}\rangle$$

$$T_2 = \frac{1}{4}\sum_{\substack{ab\\ij}} t_{ij}^{ab} \underbrace{a_a^\dagger a_b^\dagger a_j a_i}_{\hat{A}_{ij}^{ab}}$$

$$\hat{A}_{ij}^{ab} \to A_H^P$$

General exponential

$$|\Psi_0\rangle_{CC} = \prod_H\left(1+\sum_P t_H^P A_H^P\right)|\Phi_0\rangle$$

$$(A_H^P)^2|\Phi_0\rangle = 0 \qquad (A_H^P)^n|\Phi_0\rangle = 0 \quad n>1$$

$$|\Psi_0\rangle_{CC} = \exp(T)\,|\Phi_0\rangle$$

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

$$\frac{1}{(2!)^2}$$

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

$$= t_{ji}^{ba}$$

$$\langle ab||ij\rangle_{AS} = -\langle ab||ji\rangle_{AS} - \ldots$$

MBPT(2)

2p2h

$$t_{ij}^{ab} = \frac{\langle ab||ij\rangle_{AS}}{\varepsilon_i+\varepsilon_j-\varepsilon_a-\varepsilon_b}$$

$$T_3 = \frac{1}{(3!)^2} \sum_{\substack{abc \\ ijk}} t_{ijk}^{abc} \left(a_a^+ a_b^+ a_c^+ a_k a_j a_i \right)$$

CC FCI

$$e^{T} |\Phi_0\rangle \qquad \sum_{PH} C_H^P |\Phi_0\rangle = \sum_{\lambda=0}^{\infty} c_\lambda |\Phi_\lambda\rangle$$

$$T = T_1 + T_2 + \dots + T_{NDNH}$$

$$\underline{C_0} = \underline{1} = C_{0H}^{0P}$$

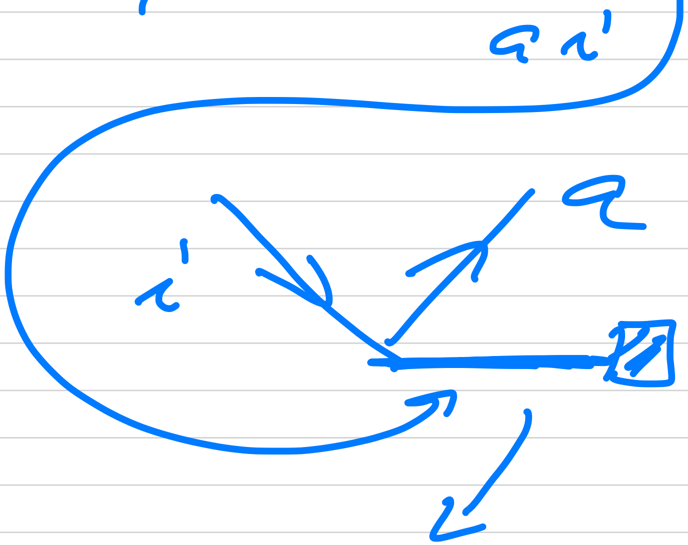
$$\underline{T_1} = C_{1H}^{1P} = \underline{C_1}$$

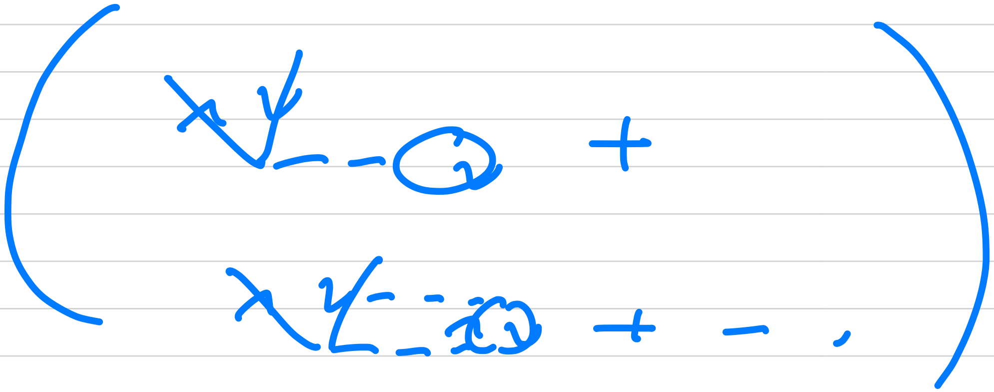
$$T_2 + \frac{1}{2} T_1^2 = C_2 \left(= C_{2H}^{2P} \right)$$

$$C_3 = T_3 + T_1 T_2 + \frac{1}{6} T_1^3 \quad (3p3h)$$

$$\left(\exp(T) \right)$$

$$T_1 = \sum_{ai} t_i^a \, a_a^\dagger a_i$$





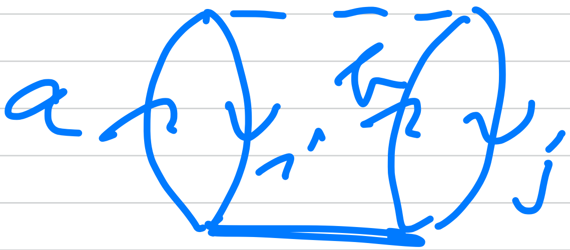
$$\text{MBPT}(2): \quad \frac{\langle a|f|i\rangle}{\varepsilon_i - \varepsilon_a}$$

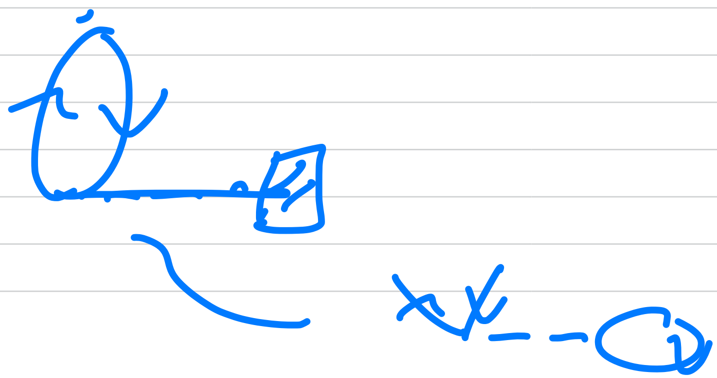
$$C_2 = T_2 + \frac{1}{2} T_1^2$$

$T_2 =$

$$= \frac{1}{4} \sum_{abij} t_{ij}^{ab} \, a_a^\dagger a_b^\dagger a_j a_i$$

$\frac{1}{2} T_1^2$;





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

$$\hat{H}|\Psi_0\rangle_{CC} = E_0|\Psi_0\rangle_{CC}$$

$$H e^T|\Phi_0\rangle = E_0 e^T|\Phi_0\rangle$$

$$E_{min} = \underset{t_H^P}{\mathrm{argmin}} \frac{\langle\Phi_0|e^{-T}He^T|\Phi_0\rangle}{\underbrace{\langle\Psi_0|\Psi_0\rangle}_{\langle\Phi_0|\Phi_0\rangle}}$$

non-linear dependence on t_H^P; in principle this leads to an intractable set of non-linear equations:

Equations (projection approach)

$$\hat{H} e^{T} |\Phi_0\rangle = E_0 \underbrace{e^{T} |\Phi_0\rangle}_{|\Psi_0\rangle}$$

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

$$\langle \Phi_0 | \Psi_0 \rangle = 1$$

Think to FCI: First row

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

$$\Delta E_0 = E_0 - E_0^{REF} = \sum_{PH>0} \langle \Phi_0 | H | \Phi_H^P \rangle \times C_H^P$$

$$=$$

$$\Delta E_0 = \sum_{ai} c_i^a \langle a|f|i\rangle + \sum_{\substack{ab\\ij}} c_{ij}^{ab} \langle ab \| ij\rangle$$

$$\langle \Phi_i^a | \hat{H} e^T | \Phi_0 \rangle = E_0 \langle \Phi_i^a | e^T | \Phi_0 \rangle$$

For a truncated $T \simeq \underbrace{T_1 + T_2}_{\text{CCSD}}$

(i) $\langle \Phi_0 | \mathcal{H} e^{T} | \Phi_0 \rangle = E_0$

(ii) $\langle \Phi_i^a | \mathcal{H} e^{T} | \Phi_0 \rangle =$

$E_0 \langle \Phi_i^a | e^{T} | \Phi_0 \rangle$

(iii) $\langle \Phi_{ij}^{ab} | \mathcal{H} e^{T} | \Phi_0 \rangle$

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

$$\hat{\mathcal{H}} = E_0^{Ref} + \underbrace{\hat{F}_N + \hat{V}_N}_{\mathcal{H}_N}$$

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

$$\underbrace{\left(e^{T}|\Phi_c\rangle\right)}_{|\Psi_0\rangle}$$

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

(i)

$$= \langle \Phi_c | e^{-T} \mathcal{H}_N e^{T} | \Phi_c \rangle$$

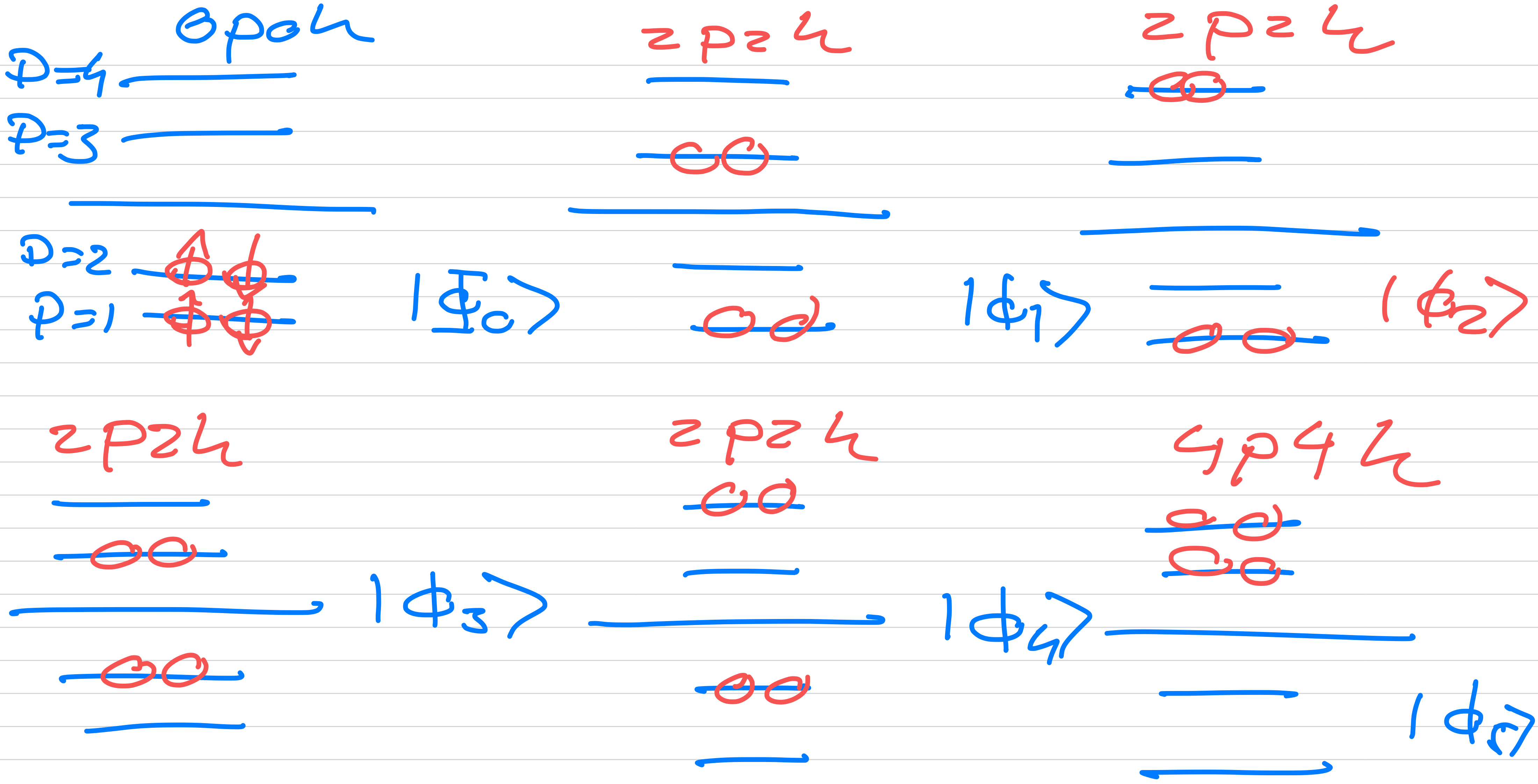
(ii) $\langle \Phi_i^a | e^{-T} \mathcal{H}_N e^{T} | \Phi_c \rangle = 0$

(iii) $\langle \Phi_{ij}^{ab} | e^{-T} \mathcal{H}_N e^{T} | \Phi_0 \rangle = 0$

FCI

$\langle 0p0h | H | 1p1h \rangle$

$$
\begin{array}{c|cccccc}
 & 0p0h & 1p1h & 2p2h & \cdots & & NpNh \\
\hline
0p0h & \tilde{X} & \tilde{X} & \tilde{X} & 0 & 0 & 0 \\
1p1h & 0^{cc} & \tilde{X} & \tilde{X} & & & \\
2p2h & 0^{cc} & \tilde{X} & \tilde{X} & & & \\
\vdots & 0 & \tilde{X} & \tilde{X} & & & \\
\vdots & \vdots & & \tilde{X} & & & \\
\vdots & \vdots & & & & & \\
NpNh & & & & & &
\end{array}
$$



→ Hamiltonian matrix

6×6

$$|\Psi_0\rangle = c_0 |\Phi_0\rangle + c_1 |\Phi_1\rangle + \ldots + c_r |\Phi_r\rangle$$

$$|\Psi_0^{(1)}\rangle = \cancel{\sum_{ai} |\Phi_i^a\rangle \frac{\langle a|f|i\rangle}{\varepsilon_i - \varepsilon_a}}$$

1p1h

$$+ \frac{1}{4} \sum_{\substack{ab \\ ij}} |\Phi_{ij}^{ab}\rangle \frac{\langle ab|v|ij\rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$

2p2h