FYS4480/9480, lecture
October 30, 2025

FYS4480/9480 October 30

MBPT

$$|\Psi_0\rangle = c_0|\Phi_0\rangle + \sum_{ai} c_i^a|\Phi_i^a\rangle + \sum_{abij} c_{ij}^{ab}|\Phi_{ij}^{ab}\rangle + \dots + \dots + NPNH$$

$$= c_0|\Phi_0\rangle + \sum_{\lambda=1}^{\infty} c_\lambda|\Phi_\lambda\rangle$$

$$\mathcal{H}|\Psi_0\rangle = (\mathcal{H}_0 + \mathcal{H}_I)|\Psi_0\rangle$$

$$\langle\Phi_0|\mathcal{H}|\Psi_0\rangle = \langle\Phi_0|\mathcal{H}_0 + \mathcal{H}_I|\Psi_0\rangle$$

$$E_0 = \langle \Phi_0 | \mathcal{H}_0 | \Phi_0 \rangle$$

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

$c_0 = 1$

$$\mathcal{H}_0 |\Phi_0\rangle = E_0 |\Phi_0\rangle$$

$$\langle \Psi_0 | \mathcal{H}_0 | \Phi_0 \rangle = \langle \Phi_0 | \mathcal{H}_0 | \Psi_0 \rangle^*$$

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

$$\Delta E_0 = E_0 - E_0$$

correlation energy

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

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

$$\Delta E_{FCI}' = \sum_{ai} \left(c_i^{\hat{a}} \underbrace{\langle a | f | i \rangle}_{\langle \Phi_i^a | H | \Phi_0 \rangle \leftarrow 1p1h} \right)$$

$$+ \sum_{\substack{ab \\ ij}} \left(c_{ij}^{\widehat{ab}} \underbrace{\langle ab | v | ij \rangle_{AS}}_{\langle \Phi_{ij}^{ab} | H | \Phi_0 \rangle \leftarrow 2p2h} \right)$$

non-degenerate $|\Phi_0\rangle$

projection $\hat{P} = |\Phi_0\rangle\langle\Phi_0|$

(model space or effective Hilbert space)

$$\hat{Q} = \sum_{i=1}^{\infty} |\Phi_i\rangle\langle\Phi_i|$$

$$\hat{P}^2 = \hat{P} \quad , \quad \hat{Q}^2 = \hat{Q}$$

$$\hat{P}\hat{Q} = \hat{Q}\hat{P} = 0 \quad , \quad [\hat{P}, \hat{Q}] = 0$$

$$[\hat{P}, \hat{H}_0] = [\hat{Q}, \hat{H}_0] = 0$$

From last week

$$|\Psi_0\rangle = \sum_{n=0}^{\infty} \left\{ \frac{\hat{Q}}{\omega - \hat{H}_0} \left(\omega - E_0 + \hat{H}_1 \right) \right\}^n \times |\Phi_0\rangle$$

$$\hat{Q}(\omega - \hat{H}_0)^{-1} =$$

$$\hat{Q}(\omega - \hat{H}_0)^{-1}\hat{Q} \quad (\hat{Q}^2 = \hat{Q})$$

$$\frac{\hat{Q}}{\omega - \hat{H}_0} = \sum_{\lambda=1}^{\infty} \frac{|\Phi_\lambda\rangle\langle\Phi_\lambda|}{\omega - \hat{H}_0}$$

$$\hat{H}_0|\Phi_\lambda\rangle = \varepsilon_\lambda|\Phi_\lambda\rangle$$

$$\Delta E_0 = E_0 - \mathcal{E}_0 = \langle \Phi_0 | H_1 | \Psi_0 \rangle$$

$$= \sum_{n=0}^{\infty} \langle \Phi_0 | H_I \left\{ \frac{\hat{P}}{\omega - H_0} (\omega - E_0 + H_I) \right\}^n$$

$$\times | \Phi_0 \rangle$$

(i) Brillouin – Wigner PT

(BWPT)

$$\omega = E_0$$

(ii) Rayleigh-Schrödinger PT

(RSPT) $\omega = \mathcal{E}_0$

BWPT

$$\Delta E_0 = E_0 - \mathcal{E}_0 =$$

$$\sum_{n=0}^{\infty} \langle \Phi_0 | H_I \left\{ \frac{\hat{Q}}{E_0 - H_0} H_I \right\}^n | \Phi_0 \rangle$$

$$= \underbrace{\langle \Phi_0 | H_I | \Phi_0 \rangle}_{\text{First order in } H_I}$$

$$+ \underbrace{\langle \Phi_0 | H_I \frac{\hat{Q}}{E_0 - H_0} H_I | \Phi_0 \rangle}_{\text{2nd order}} \qquad +$$

$$+ \underbrace{\langle \Phi_0 | \hat{H}_I \frac{\hat{Q}}{E_0 - H_0} \hat{H}_I \frac{\hat{Q}}{E_0 - H_0} \hat{H}_I | \Phi_0 \rangle}_{\text{3rd order in } H_I}$$

$$+ \;\ldots$$

unknown

useful lin-algebra relation

$$(A-B)^{-1} = A^{-1} + A^{-1} B (A-B)^{-1}$$

multiply from the right with $(A-B)$

$$\mathbb{1} = A^{-1}(A-B) + A^{-1} B \mathbb{1}$$

$$= \mathbb{1}$$

$$e = E_0 - H_0$$

$$\hat{Q} \frac{1}{e - \hat{Q} H_1 \hat{Q}} \hat{Q} \qquad \left(\hat{Q} \frac{1}{E_0 - H} \hat{Q} \right)$$

$$= \hat{Q} \left[\frac{1}{e} + \frac{1}{e} Q H_1 Q \frac{1}{e} + \frac{1}{e} Q H_1 Q \frac{1}{e} Q H_1 Q \frac{1}{e} + \cdots \right] \hat{Q} \qquad \Longrightarrow$$

$$\Delta E_0 = \langle \Phi_0 | \mathcal{H}_I | \Psi_0 \rangle$$

$$= \langle \Phi_0 | \mathcal{H}_1 | \Phi_0 \rangle$$

$$+ \langle \Phi_0 | \mathcal{H}_I \, Q \frac{1}{E_0 - \mathcal{H}_0 - Q \mathcal{H}_I Q} Q \mathcal{H}_1$$

$$\times | \Phi_0 \rangle$$

$$| \Psi_0 \rangle = \left(1 + Q \frac{1}{E_0 - \mathcal{H}_0 - Q \mathcal{H}_I Q} Q \mathcal{H}_I \right.$$

$$\times | \Phi_0 \rangle$$

Example

$$\mathcal{H}_0 = \sum_{p=1}^{2} \varepsilon_p \, a_p^\dagger a_p$$

$$\mathcal{H}_I = g \sum_{pq} a_p^\dagger a_q$$

$$|\Phi_0\rangle = |1\rangle = a_1^\dagger |0\rangle$$

$$|\Phi_1\rangle = |2\rangle = a_2^\dagger |0\rangle$$

$$\mathcal{H}_0 |\Phi_0\rangle = \varepsilon_1 |\Phi_0\rangle \qquad \varepsilon_1 < \varepsilon_2$$

$$\mathcal{H}_0 |\Phi_1\rangle = \varepsilon_2 |\Phi_1\rangle$$

$$\langle \Phi_0 | H_1 | \Phi_1 \rangle = g$$

$$\langle \Phi_0 | H_1 | \Phi_0 \rangle = \varepsilon_1 + g$$

$$\langle \Phi_1 | H | \Phi_1 \rangle = \varepsilon_2 + g$$

$$A = \begin{bmatrix} \varepsilon_1 + g - \lambda & g \\ g & \varepsilon_2 + g - \lambda \end{bmatrix}$$

$$\det(A) = 0$$

$$\Delta E_0 = E_0 - \varepsilon_1 =$$

$$\underbrace{\langle \Phi_0 | \mathcal{H}_I | \Phi_0 \rangle}_{g}$$

$$+ \langle \Phi_0 | \mathcal{H}_I | \underbrace{\Phi_1 \rangle \langle \Phi_1 |}_{\hat{g}} \frac{1}{E_0 - \varepsilon_2 - g}$$

$$\times \overbrace{| \phi_1 \rangle \langle}^{g} \underbrace{\Phi_1 | \mathcal{H}_1 | \Phi_0 \rangle}_{g}$$

$$E_0 - \varepsilon_1 - g = \frac{g^2}{E_0 - \varepsilon_2 - g}$$

$$(E_0 - \varepsilon_1 - g)(E_0 - \varepsilon_2 - g) - g^2 = 0$$

$$(E_0 = \lambda)$$

which is equivalent

with $\det(A) = 0$

RSPT : $w = \mathcal{E}_0$

$$\Delta E_0 = E_0 - \mathcal{E}_0 = \sum_{n=0}^{\infty} \langle \Phi_0 | \mathcal{H}_I \left\{ \frac{\hat{Q}}{\mathcal{E}_0 - \mathcal{H}_0} (\mathcal{H}_I - \Delta E_0) \right\}^n$$

$$\times | \Phi_0 \rangle$$

$$\hat{Q} \Delta E_0 | \Phi_0 \rangle = \Delta E_0 \hat{Q} | \Phi_0 \rangle = 0$$

$$\hat{Q} = \sum_{i=1}^{\infty} | \Phi_i \rangle \langle \Phi_i |$$

$$\langle \Phi_i | \Phi_j \rangle = \delta_{ij}$$

$$\Delta E_0 = \langle \Phi_0 | H_I | \Phi_0 \rangle \left(\frac{1}{2} \sum_{ij} \langle ij | v | ij \rangle_{AS} \right)$$

$$+ \underbrace{\langle \Phi_0 | H_I \frac{Q}{E_0 - H_0} \left(H_I - \underline{\Delta E_0} \right) | \Phi_0 \rangle}_{\text{2nd-order}}$$

$$+ \langle \Phi_0 | H_I \frac{Q}{E_0 - H_0} \left(H_I - \Delta E_0 \right) \frac{Q}{E_0 - H_0}$$

$$\times H_I | \Phi_0 \rangle + \dots$$

Regroup

$$\Delta E_0 = \sum_{i=1}^{\infty} \Delta E_0^{(i)}$$

$$\Delta E_0^{(1)} = \langle \Phi_0 | \mathcal{H}_I | \Phi_0 \rangle$$

$$\Delta E_0^{(2)} =$$

$$\left(\hat{e}_0 = \varepsilon_0 - \hat{\mathcal{H}}_0 \right)$$

$$= \langle \Phi_0 | \mathcal{H}_I \frac{\hat{Q}}{\hat{e}_0} \mathcal{H}_I | \Phi_0 \rangle$$

$$\Delta E_0^{(3)} = \left\langle \hat{\mathcal{H}}_I \frac{\hat{Q}}{\hat{e}_0} \hat{\mathcal{H}}_I \frac{\hat{Q}}{\hat{e}_0} \hat{\mathcal{H}}_I \right\rangle$$

$$\left(\langle \Phi_0 | \mathcal{H}_1 \cdots\cdots \mathcal{H}_I | \Phi_0 \rangle = \langle \mathcal{H}_1 \cdots \mathcal{H}_1 \rangle \right.$$

$$- \left\langle \mathcal{H}_I \frac{\hat{Q}}{\hat{e}_0} (\Delta E_0) \frac{\hat{Q}}{e_0} \mathcal{H}_I \right\rangle$$

$$\swarrow$$

$$\langle \mathcal{H}_I \rangle$$

$$= \left\langle \hat{\mathcal{H}}_I \frac{\hat{Q}}{\hat{e}_0} \mathcal{H}_I \frac{\hat{Q}}{\hat{e}_0} \mathcal{H}_I \right\rangle$$

$$- \left\langle \mathcal{H}_I \frac{\hat{Q}}{e_0^2} \mathcal{H}_I \right\rangle \langle \mathcal{H}_I \rangle$$

MBPT(2) to 2nd in H_I

$$\Delta E_0 = E_0 - \mathcal{E}_0 = \sum_{i=1}^{\infty} \Delta E_0^{(i)}$$

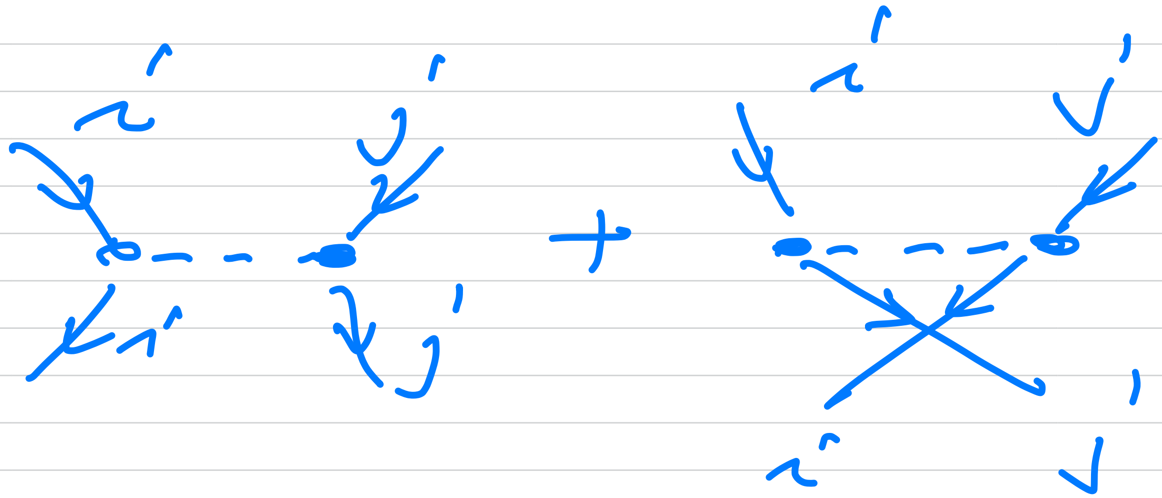
$$E_0 \simeq \underbrace{\mathcal{E}_0 + \Delta E_0^{(1)}}_{E_0^{Ref}} + \Delta E_0^{(2)}$$

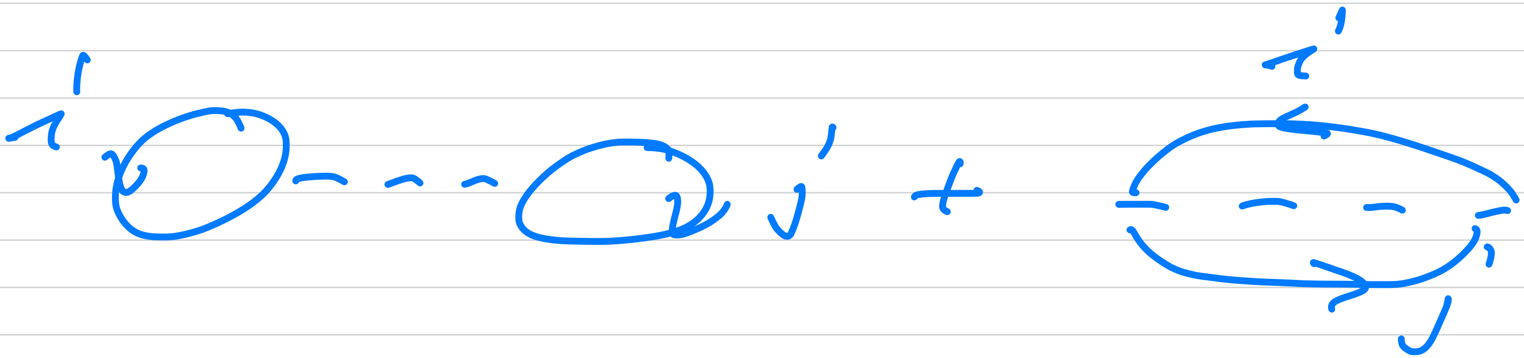
$$\langle \Phi_0 | H | \Phi_0 \rangle$$

First-order term

$$\Delta E_0^{(1)} = \frac{1}{2} \sum_{ij \leq F} \langle ij | v | ij \rangle_{AS}$$

$$\frac{1}{2}\sum_{i,j}\left\{ \langle ij|v|ij\rangle - \langle ji|v|ij\rangle \right\}$$

$$= \frac{1}{2}\sum_{ij}\Bigg\{$$  $$\Bigg\}$$

$$=$$ 

$$\Delta E_0^{(2)} = \langle \Phi_0 | \hat{H}_I \frac{\hat{Q}}{E_0 - \hat{H}_0} \hat{H}_I | \Phi_0 \rangle$$

$$= \sum_{\lambda=1}^{\infty} \frac{\langle \Phi_0 | \hat{H}_I | \Phi_\lambda \rangle \langle \Phi_\lambda | \hat{H}_I | \Phi_0 \rangle}{E_0 - E_\lambda}$$

$$\hat{H}_0 | \Phi_\lambda \rangle = E_\lambda | \Phi_\lambda \rangle$$

$$\langle \Phi_\lambda | \hat{H}_I | \Phi_0 \rangle$$

$$| \Phi_\lambda \rangle = \underbrace{| \Phi_i^a \rangle}_{1p1h} \text{ or } \underbrace{| \Phi_{ij}^{ab} \rangle}_{2p2h}$$

$$\hat{H}_0 + \hat{H}_I = \hat{H}$$

writ $|\Phi_c\rangle$

$$\hat{H} = E_0^{\text{Ref}} + \hat{F}_N + \hat{V}_N$$

$$\hat{F}_N = \sum_{pq} \langle p | \hat{h}_0 + u^{HF} | q \rangle \times a_p^\dagger a_q$$

$$\hat{u}^{HF} = \sum_{pq} \langle p | u^{HF} | q \rangle a_p^\dagger a_q$$

$$= \sum_{pq} a_p^\dagger a_q \sum_{j \le F} \langle pj | v | qj \rangle_{AS}$$

$$\hat{H}_I = \sum_{pq} \langle p | u^{HF} | q \rangle a_p^\dagger a_q$$

$$+ \frac{1}{4} \sum_{pqrs} a_p^\dagger a_q^\dagger a_s a_r$$

$$\times \langle pq | w | rs \rangle_{AS}$$

$$\sum_{pq} \langle \Phi_i^a | a_p^\dagger a_q | \Phi_0 \rangle \langle p | u^{HF} | q \rangle$$

$|\Phi_i^a\rangle$ is one of the intermediate states in $\sum_{\lambda=1}^{\infty} |\Phi_\lambda\rangle\langle\Phi_\lambda|$

$$\langle \Phi_i^a | a_p^\dagger a_q | \Phi_0 \rangle =$$

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

$$\delta_{pa} \delta_{qi}$$

1p1h term gives to 2nd order

$$\sum_{ai} \frac{\langle i | u^{HF} | a \rangle \langle a | u^{HF} | i \rangle}{\varepsilon_0 - \varepsilon_i^a}$$

$$\varepsilon_i^a = \varepsilon_a - \varepsilon_i + \varepsilon_0$$

$$= \sum_{ai} \frac{|\langle a | u^{HF} | i \rangle|^2}{\varepsilon_i - \varepsilon_a}$$

SP-energier

$$= \sum_{aij} \frac{|\langle aj | v | ij \rangle_{AS}|^2}{\varepsilon_i - \varepsilon_a}$$

FCI Term for $\hat{F}_N$

$$\sum_{ai} C_i^a \langle a | f | i \rangle$$

$$\text{MBPT}(2): \sum_{ai} \frac{\langle i | u^{HF} | a \rangle}{\varepsilon_i - \varepsilon_a} \langle a | u^{HF} | i \rangle$$

$$\text{FCI}: \sum_{ai} c_i^a \left(\langle i | \cancel{h_0} | a \rangle^{=0} + \langle i | u^{HF} | a \rangle \right)$$

$$\hat{h}_0 | a \rangle = \varepsilon_a | a \rangle$$

$$\langle a | i \rangle = 0$$

$$= \sum_{ai} c_i^a \langle a | u^{HF} | i \rangle$$

in MBPT(2)

1PI2

$$c_i^a = \frac{\langle i | u^{HF} | a \rangle}{\varepsilon_i - \varepsilon_a}$$