# Lecture Fys4480, November 3, 2023

FCI

$$\Delta E = E_0 - E_0^{Ref} = \underbrace{\sum_{ai} c_i^a \langle i|\hat{f}|a\rangle}^{1p1h}$$

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

$$+ \underbrace{\sum_{\substack{ab\\ij}} c_{ij}^{ab} \langle ij|v|ab\rangle_{AS}}_{2p2h}$$

MBPT

$$h_0|p\rangle = \varepsilon_p|p\rangle$$

$$H_0|\Phi_0\rangle = W_0|\Phi_0\rangle = \left\{\sum_{i\leq F} \varepsilon_i\right\}|\Phi_0\rangle$$

$$H = H_0 + H_I$$

$$\hat{P} = |\Phi_0\rangle\langle\Phi_0| \qquad \hat{Q} = \sum_{M=1}^{\infty} |\Phi_M\rangle\langle\Phi_M|$$

$$\hat{P}^2 = \hat{P} \qquad \hat{Q}^2 = \hat{Q} \qquad [P, Q] = 0$$

$$|\Psi_0\rangle = |\Phi_0\rangle + \sum_{M=1}^{\infty} c_M |\Phi_M\rangle$$

$$= |\Phi_0\rangle + \sum_{PH} c_H^P |\Phi_H^P\rangle$$

$$[P, H_0] = [Q, H_0] = 0$$

$$H|\Phi_0\rangle \neq E_0|\Phi_0\rangle$$

$$H|\Psi_0\rangle = E_0|\Psi_0\rangle$$

$$\langle\Phi_0|\overset{\sim H_0 + H_I}{H}|\Psi_0\rangle = E_0\langle\Phi_0|\Psi_0\rangle = E_0$$

subtract $\langle\Psi_0|H_0|\Phi_0\rangle = W_0$

$$\Delta E = E_0 - W_0 = \langle \Phi_0 | H_1 | \Psi_0 \rangle$$

$$|\Psi_0\rangle = (\hat{P} + \hat{Q})|\Psi_0\rangle =$$

$$\left( |\Phi_0\rangle\langle\Phi_0| + \hat{Q} \right)\left( |\Phi_0\rangle + \sum_M C_M |\Phi_M\rangle \right)$$

$$= |\Phi_0\rangle + \hat{Q}|\Psi_0\rangle$$

Add and subtract $w|\Psi_0\rangle$

$$(w - H_0)|\Psi_0\rangle = (w - E_0 + H_1)|\Psi_0\rangle$$

$w - H_0$ is invertible

$$|\Psi_0\rangle = \frac{1}{\omega - H_0}(\omega - E_0 + H_1)|\Psi_0\rangle$$

$$Q|\Psi_0\rangle = Q\frac{1}{\omega - H_0}(\omega - E_0 + H_1)|\Psi_0\rangle$$

$$\hat{Q}^2 = \hat{Q} \qquad [Q, H_0] = 0$$

$$Q^2\left[\frac{1}{\omega}\left(1 + \frac{H_0}{\omega} + \frac{H_0^2}{\omega^2} + \cdots\right)\right]$$

$$= Q\frac{1}{\omega}\left(1 + \frac{H_0}{\omega} + \frac{H_0^2}{\omega^2} + \cdots\right)Q$$

$$= \frac{Q}{\omega - H_0} = \frac{\sum_M |\phi_M\rangle\langle\phi_M| \hat{H}_0}{\omega - H_0 \, \hat{H}_0} \qquad \hat{Q} = \sum_{M=1} |\phi_M\rangle\langle\phi_M|$$

$$H_0 |\Phi_M\rangle = W_M |\Phi_M\rangle$$

$$|\Psi_0\rangle = |\Phi_0\rangle + \frac{Q}{\omega - H_0}(\omega - E_0 + H_1)|\Psi_0\rangle$$

solved iteratively

$$|\Psi_0^{(0)}\rangle = |\Phi_0\rangle$$

$$|\Psi_0^{(1)}\rangle = |\Phi_0\rangle + \frac{Q}{\omega - H_0}(\omega - E_0 + H_1)|\Phi_0\rangle$$

$$|\Psi_0^{(2)}\rangle = |\Phi_0\rangle + \text{———} \quad \text{———} |\Psi_0^{(1)}\rangle$$

$$= |\Psi_0\rangle = \sum_{i=0}^{\infty} \left\{ \frac{Q}{\omega - H_0}(\omega - E_0 + H_1) \right\}^i |\Phi_0\rangle$$

$$\Delta E = \langle \Phi_0 | H_1 | \Psi_0 \rangle$$

$$= \sum_{i=0}^{\infty} \langle \Phi_0 | H_1 \left\{ \frac{Q}{\omega - \hat{H}_0} (\omega - E_0 + H_1) \right\}^i | \Phi_0 \rangle$$

(i) Brillouin-Wigner pert theory

$$\omega = E_0$$

$$\Delta E = \underbrace{\langle \Phi_0 | H_1 | \Phi_0 \rangle}_{\text{1st order in } H_I} + \underbrace{\langle \Phi_0 | H_1 \frac{Q}{E_0 - H_0} H_1 | \Phi_0 \rangle}_{\text{2nd order}}$$

$$+ \underbrace{\langle \Phi_0 | H_1 \frac{Q}{E_0 - H_0} H_1 \frac{Q}{E_0 - H_0} H_1 | \Phi_0 \rangle}_{\text{3rd order}} + \cdots$$

(ii) Rayleigh-Schrödinger

$$\omega = W_0$$

$$\Delta E = \sum_{i=0}^{\infty} \langle \Phi_0 | H_1 \left\{ \frac{Q}{W_0 - H_0} (H_1 - \Delta E) \right\}^i | \Phi_0 \rangle$$

$$\omega - E_0 + H_1 \qquad \omega = W_0 \qquad \sum_M |\Phi_M\rangle\langle\Phi_M|\Phi_0\rangle$$

$$\Delta E = E_0 - W_0 \qquad Q \Delta E | \Phi_0 \rangle$$

$$\Delta E = \sum_{i=1}^{\infty} \Delta E^{(i)} \qquad = 0$$

$$\Delta E^{(1)} = \langle \Phi_0 | H_1 | \Phi_1 \rangle$$

$$\Delta E^{(2)} = \langle \Phi_0 | H_1 \frac{Q}{W_0 - H_0} (H_1 - \underbrace{\Delta E}_{=0}) | \Phi_0 \rangle$$

$$\Delta E^{(3)} = \langle \Phi_0 | H_1 \frac{Q}{W_0 - H_0} (H_1 - \Delta E) \frac{Q}{W_0 - H_0} H_1 | \Phi_0 \rangle$$

$$\langle \Phi_0 | H_1 | \Phi_0 \rangle$$

$$= \langle \Phi_0 | H_1 \frac{Q}{W_0 - H_0} H_1 \frac{Q}{W_0 - H_0} H_1 | \Phi_0 \rangle$$

$$- \langle \Phi_0 | H_1 \frac{Q}{W_0 - H_0} \Delta E^{(1)} \frac{Q}{W_0 - H_0} H_1 | \Phi_0 \rangle$$

First and 2nd-order pert theory

$$\Delta E^{(1)} = \langle \Phi_0 | H_1 | \Phi_0 \rangle$$

$$\Delta E(MBPT(1)) = \Delta E^{(1)}$$

$$E_0^{Ref}(MBPT) = W_0$$

$$W_0 + \Delta E^{(1)} = E_0^{Ref}(FCI)$$

$$\Delta E^{(2)} = \langle \Phi_0 | H_1 \frac{Q}{W_0 - H_0} H_1 | \Phi_0 \rangle$$

$$= \sum_{M=1}^{\infty} \langle \Phi_0 | H_1 \frac{|\Phi_M\rangle\langle\Phi_M|}{W_0 - H_0} H_1 | \Phi_0 \rangle$$

$$= \sum_{M=1}^{\infty} \frac{\langle \Phi_0 | H_1 | \Phi_M \rangle \langle \Phi_M | H_1 | \Phi_0 \rangle}{\omega_0 - \omega_M}$$

$$|\Phi_M\rangle = \left\{ |\Phi_i^a\rangle , \; |\Phi_{ij}^{ab}\rangle \right\}$$

$$\quad 1p1h \qquad\qquad 2p2h$$

$$\langle \Phi_0 | H_1 | \Phi_M \rangle$$

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

$$\hat{F}_N = \sum_{pq} \langle p | f | q \rangle a_p^{\dagger} a_q$$

$$\langle p | f | q \rangle = \langle p | h_0 | q \rangle + \sum_{j \le F} \langle pj | v | qj \rangle_{AS}$$

Here we have

$$\langle p | h_0 | q \rangle = \varepsilon_p \delta_{pq}$$

$$V_N = \frac{1}{4} \sum_{pqrs} \langle pq | v | rs \rangle_{AS} \, a_p^\dagger a_q^\dagger a_s a_r$$

$$\langle \Phi_0 | H_1 | \Phi_M \rangle = \langle \Phi_0 | F_N + V_N | \Phi_M \rangle$$

$$\langle \Phi_0 | \sum_{pq} \langle p | f | q \rangle \underbrace{a_p^\dagger a_q}_{a_p^\dagger a_q a_a^\dagger a_i} \underbrace{| \Phi_M \rangle}_{|\Phi_i^a\rangle}$$

$$\langle \Phi_0 | a_p^\dagger a_q^\dagger a_j a_r | \underbrace{\Phi_M}_{a_a^\dagger a_b^\dagger a_j a_i} \rangle$$

$$= \langle ij | v | ab \rangle$$

$$\Rightarrow$$

$$\Delta E^{(2)} = \underbrace{\sum_{ai}}_{M = |p1h} \frac{\overbrace{|\langle i | f' | a \rangle|^2}^{\sum_j \langle ij' | v | aj \rangle_{AS}}}{\varepsilon_i - \varepsilon_a} +$$

$$w_0 - \underline{w_M} \quad (w_M = \varepsilon_a - \varepsilon_i + w_0)$$

$$\frac{1}{4}\sum_{\underbrace{\substack{ab\\ij}}_{2p2h}} \frac{|\langle ij|v|ab\rangle_{AS}|^2}{\varepsilon_i+\varepsilon_j-\varepsilon_a-\varepsilon_b}$$

$$|\Phi_M\rangle = \{|\Phi_{ij}^{ab}\rangle\}$$

$$W_M = ?$$

$$H_0|\Phi_{ij}^{ab}\rangle = (\varepsilon_a+\varepsilon_b-\varepsilon_j-\varepsilon_i + W_0)$$

FCI:

$$E_0^{ref} = \langle\Phi_0|H|\Phi_0\rangle = \underbrace{\langle\Phi_0|H_0|\Phi_0\rangle}_{W_0} + \underbrace{\langle\Phi_0|H_1|\Phi_0\rangle}_{\Delta E^{(1)}}$$

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

$\langle i|h_0|a\rangle = 0$

$$t_i^a(1) = \frac{\langle a|f|i\rangle}{\varepsilon_i - \varepsilon_a}$$

$$t_{ij}^{ab}(1) = \frac{\langle ab|v|ij\rangle_{AS}}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$

$$\Delta E(2) = \sum_{ai} t_i^a(1)\langle i|f|a\rangle$$

$$+ \frac{1}{4}\sum_{\substack{ab\\ij}} t_{ij}^{ab}(2)\langle ij|v|ab\rangle_{AS}$$

$$\Delta E(FCI) = \sum_{ai} C_i^a \langle i|f|a\rangle +$$

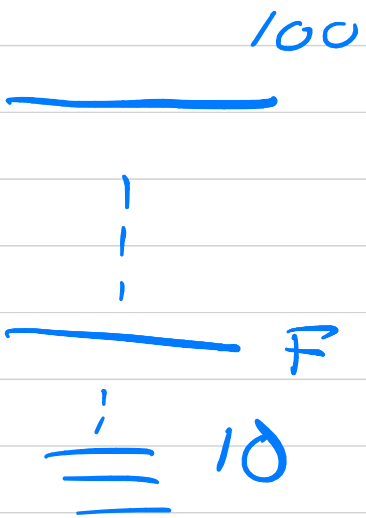
$$\sum_{\substack{ab\\ij}} C_{ij}^{ab}\langle ij|v|ab\rangle_{AS}$$

$m = 100$

$N = 10$ $\Rightarrow$ $\# SD = \binom{m}{N} = \dfrac{m!}{(m-N)!\,N!}$

$\gg 10^{10}$ computational limit for FCI calculations.

MBPT




$$\sum_{\underbrace{a}_{90}\,\underbrace{i}_{10}} t_i^a(i) \langle i|f|a\rangle$$

$$+ \sum_{\underbrace{ab}_{\sim 100^2}\,\underbrace{ij}_{\sim 10^2}} t_{ij}^{ab}(i) \langle ij|v|ab\rangle_{AS}$$

computational issues

$$\sum_{\substack{ab\\ij}} t_{ij}^{ab}(1) \langle ij|v|ab\rangle = \sum_{IJ} T_{JI} V_{IJ}$$
$$= TV$$

$I = \{(ij)\}$ possible 2h configurations

$J = \{(ab)\}$ possible 2p configurations $(a \leq b)$

$$V_{IJ} = \langle ij|v|ab\rangle_{AS}$$

$$T_{JI} = \langle ab|\hat{t}|ij\rangle = \frac{\langle ab|v|ij\rangle}{\varepsilon_i+\varepsilon_j-\varepsilon_a-\varepsilon_b}$$