FYS4480, OCT 28, 2022

$$\hat{P}^2 = \hat{P} = |\Phi_0\rangle\langle\Phi_0| \quad \text{(model space)}$$

$$\hat{H}_0|\Phi_0\rangle = W_0|\Phi_0\rangle$$

$$W_0 = \sum_{i\le F} \varepsilon_i$$

$$\hat{Q}^2 = \hat{Q} = \sum_{m\neq 0} |\Phi_m\rangle\langle\Phi_m|$$

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

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

FCI

$$E_0^{Ref} = W_0 + \langle\Phi_0|H_I|\Phi_0\rangle$$

$$= \sum_i \langle i|\hat{h}_0|i\rangle + \frac{1}{2}\sum_{ij}\langle ij|\hat{v}|ij\rangle_{AS}$$

$$= \sum_i \langle i|\hat{f}|i\rangle + -1 -$$

$$\Delta E = E - E_0^{Ref} = \text{correlation energy.}$$

$$\Delta E = \sum_{ai} C_i^a \langle i|f|a\rangle + \sum_{\substack{ab\\ ij}} C_{ij}^{ab}\langle ij|v|ab\rangle_{AS}$$

MBPT

$$\Delta E = E - W_0$$

$$|\Psi_0\rangle = |\Phi_0\rangle + \sum_m C_{om} |\Phi_m\rangle$$

$$= \sum_{i=0}^{\infty} \left\{ \frac{Q}{W - \hat{H}_0} (W - E + H_I) \right\}^i |\Phi_0\rangle$$

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

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

Brillouin-Wigner pert theory (BW)

$$\omega = E$$

$$\Delta E = \langle \Phi_0 | H_1 + H_1 Q \frac{1}{E - \hat{H}_0} Q H_1$$

$$+ H_1 Q \frac{1}{E - \hat{H}_0} Q H_1 Q \frac{1}{E - \hat{H}_0} Q H_1 +$$

$$\cdots |\Phi_0\rangle$$

$$|\Psi_0\rangle = \Big(1 + Q\frac{1}{E-H_0}QH_I$$

$$+ Q\frac{1}{E-H_0}QH_I Q\frac{1}{E-H_0}QH_I$$

$$+ \ldots \Big)|\Phi_0\rangle$$

Define the wave operator

$$\Omega_E = 1 + Q\frac{1}{E-H_0}QH_1 +$$

$$Q\frac{1}{E-H_0}QH_1 Q\frac{1}{E-H_0}QH_I$$

$$+ \ldots$$

$$\hat{H}_1\hat{\Omega}_E = \hat{H}_{eff}$$

$$|\Psi_0\rangle = \Omega_E|\Phi_0\rangle$$

$$\Delta E = \langle\Phi_0|H_I\Omega_E|\Phi_0\rangle$$

$$E = W_0 + \langle\Phi_0|H_I\Omega_E|\Phi_0\rangle$$

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

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

$$= \frac{1}{2}\sum_{ij}\langle ij|v|ij\rangle_{AS}$$

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

$$\Delta E(FCI) = \sum_{i=2}^{\infty} \Delta E^{(i)}$$

$$\Delta E^{(2)} = \sum_{m \neq 0} \frac{\langle \Phi_0 | H_1 | \Phi_m \rangle \langle \Phi_m | H_1 \times | \Phi_0 \rangle}{E - W_m}$$

$$Q \frac{1}{E - H_0} Q$$

$$H_0 | \Phi_m \rangle = W_m | \Phi_m \rangle$$

$$\Delta E^{(3)} = \sum_{\substack{m,n \\ \neq 0}} \frac{\langle \Phi_0 | H_1 | \Phi_m \rangle \langle \Phi_m | H_1 | \Phi_n \rangle \times \langle \Phi_n | H_1 | \Phi_0 \rangle}{(E - W_m)(E - W_n)}$$

wave operator

$$\Omega_E^{(1)} = \sum_{m \neq 0} \frac{| \Phi_m \rangle \langle \Phi_m | H_1 | \Phi_0 \rangle}{E - W_m}$$

$$\Delta E = \langle \Phi_0 | H_1 + Q \frac{1}{E - H_0 - QH_1Q} Q H_1 | \Phi_0 \rangle$$

Rayleigh-Schrödinger theory (RS)

$$\omega = W_0$$

$\omega - E$

$$\Delta E = \sum_{n=0}^{\infty} \langle \Phi_0 | H_1 \left\{ \frac{Q}{W_0 - \hat{H}_0} (H_1 - \Delta E) \right\}^{n} \times | \Phi_0 \rangle$$

$$\left(\hat{Q} \Delta E | \Phi_0 \rangle = 0 \right)$$

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

$$+ \langle \Phi_0 | H_1 \frac{Q}{W_0 - \hat{H}_0} (H_1 - \Delta E) | \Phi_0 \rangle$$

$$+ \langle \Phi_0 | H_1 \frac{Q}{W_0 - \hat{H}_0} (H_1 - \Delta E) \frac{Q}{W_0 - \hat{H}_0} \times H_1 | \Phi_0 \rangle + \cdots$$

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

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

$$\Delta E^{(2)} = \sum_m \frac{\langle \Phi_0 | H_1 | \phi_m \rangle \langle \Phi_m | \times H_1 | \phi_0 \rangle}{w_0 - w_m}$$

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

$$\vdots$$

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

$$\Delta E^{(2)} = \sum_{m \neq 0} \frac{\langle \Phi_0 | H_1 | \Phi_m \rangle \langle \Phi_m | H_1 | \Phi_0 \rangle}{W_0 - W_m}$$

$$|\Phi_m\rangle = \sum_{ai} |\Phi_i^a\rangle \quad 1p1h$$

$$|\Phi_i^a\rangle = a_a^\dagger a_i |\Phi_0\rangle$$

or

$$\sum_{\substack{ab\\ij}} |\Phi_{ij}^{ab}\rangle$$

$$a_a^\dagger a_b^\dagger a_j a_i |\Phi_0\rangle$$

(i) $|\Phi_m\rangle = |\Phi_i^a\rangle$

$$\sum_m |\Phi_m\rangle\langle\Phi_m|$$

$$= \sum_{ai} |\Phi_i^a\rangle\langle\Phi_i^a|$$

$$\Delta E^{(2)} = \sum_{ai} \frac{\langle \Phi_0 | H_1 | \Phi_i^a \rangle \langle \Phi_i^a | H_I | \Phi_0 \rangle}{W_0 - \underline{W_m}}$$

$$H_0 |\Phi_i^a\rangle = W_0 - \varepsilon_i + \varepsilon_a$$

$$\Delta E^{(2)} = \sum_{ai} \frac{|\langle \Phi_0 | H_I | \Phi_i^a \rangle|^2}{\varepsilon_i - \varepsilon_a}$$

$$H_I = \sum_{pq} a_p^\dagger a_q \sum_j \langle pj | v | qj \rangle_{AS}$$

$$+ \frac{1}{4} \sum_{\substack{pq\\rs}} a_p^\dagger a_q^\dagger a_s a_r \times \langle pq | v | rs \rangle_{AS}$$

$$\langle \Phi_0 | a_p^\dagger a_q a_a^\dagger a_i | \Phi_0 \rangle = \delta_{qa} \delta_{pi}$$

$$\langle \Phi_0 | a_p^\dagger a_q^\dagger a_a a_s a_a^\dagger a_i | \Phi_0 \rangle \to 0$$

$$\Delta E^{(2)} = \sum_{ai} \frac{\left|\sum_j \langle ij | v | aj \rangle_{AS}\right|^2}{\varepsilon_i - \varepsilon_a}$$

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

(ii) $|\Phi_m\rangle = |\Phi_{ij}^{ab}\rangle$

$$\sum_m \Rightarrow \sum_{\substack{ab\\ij}}$$

$$\sum_{\substack{ab\\ij}} \frac{|\langle \Phi_0|H_1|\Phi_{ij}^{ab}\rangle|^2}{\varepsilon_i+\varepsilon_j-\varepsilon_a-\varepsilon_b}$$

$$\langle \Phi_0|H_1\, a_a^\dagger a_b^\dagger a_j a_i|\Phi_0\rangle \qquad \langle pq|v|rs\rangle$$

$$a_p^\dagger a_q^\dagger a_s \; a_r \; a_a^\dagger a_b^\dagger a_j a_i$$

(1) $\qquad \langle ij|v|ab\rangle_{AS}$

$-\langle ij|v|ba\rangle_{AS}$

$\langle ji|v|ba\rangle_{AS}$

$-\langle ji|v|ab\rangle_{AS}$

$$\Delta E^{(2)} = \frac{1}{4}\sum_{\substack{ab\\ij}} \frac{\langle ij|v|ab\rangle\langle ab|v|ij\rangle}{\varepsilon_i+\varepsilon_j-\varepsilon_a-\varepsilon_b}$$

collect

$$\Delta E^{(2)}: \quad \sum_{ai} \frac{\langle i|w^{HF}|a\rangle\langle a|w^{HF}|i\rangle}{\varepsilon_i-\varepsilon_a}$$

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

$$E_{RS}^{(2)} = W_0 + \Delta E^{(1)} + \Delta E^{(2)}$$

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

$$+ \sum_{\substack{ab \\ ij}} C_{ij}^{ab} \langle ij|v|ab\rangle$$

FCI

$$C_{ij}^{ab} \overset{\text{MBPT}}{\approx} \frac{\langle ab|v|ij\rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$

$$\langle i|f|a\rangle = \langle i|h_0|a\rangle + \sum_j \langle ij|v|aj\rangle$$

$$= \underbrace{\langle i|h_0|a\rangle}_{=0} + \langle i|u^{HF}|a\rangle$$

FCI

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