Lecture October 31, 2024, FYS4480/9480

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correction to example from oct 25

$$\det\begin{bmatrix} \varepsilon_1 + g - \lambda & g \\ g & \varepsilon_2 + g - \lambda \end{bmatrix} = 0$$

Lowest-lying state

$$\lambda_1 = \frac{\varepsilon_1 + \varepsilon_2}{2}\left[1 + \frac{2g}{\varepsilon_1 + \varepsilon_2} - \right.$$

$$\left[\frac{\sqrt{(\varepsilon_1-\varepsilon_2)^2+4g^2}}{2}\right]$$

$$\left((1+x)^{1/2} = 1+\frac{x}{2}-\frac{x^2}{8}+\dots\right)$$

$$x = \left(\frac{2g}{(\varepsilon_1-\varepsilon_2)}\right)^2$$

$$\lambda_1 = \varepsilon_1 + \underbrace{g}_{\text{1st order PT}}$$

$$+ \underbrace{\frac{g^2}{\varepsilon_1-\varepsilon_2}}_{\text{2nd order PT}} - \underbrace{\frac{g^4}{(\varepsilon_1-\varepsilon_2)^3}}_{\text{4th-order PT}} + O(g^5)$$

Many-body PT (MBPT)

$$|\Psi_0\rangle = c_0 |\Phi_0\rangle + \sum_{i=1}^{\infty} c_i |\Phi_i\rangle$$

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

$$H = H_0 + H_I$$

$$H|\Psi_0\rangle = (H_0 + H_1)|\Psi_0\rangle$$

$$\langle \Phi_0 |$$

$$\langle \Phi_0 | H | \Psi_0 \rangle = \langle \Phi_0 | H_0 + H_1 | \Psi_0 \rangle$$

$$\mathcal{E}_0 = \langle \Phi_0 | H_0 | \Phi_0 \rangle$$

$$\langle \Phi_0 | \Phi_0 \rangle = \underline{1} \quad \wedge \quad \langle \Phi_0 | \Psi_0 \rangle = \underline{1}$$

$$\langle \Psi_0 | H_0 | \Phi_0 \rangle = \mathcal{E}_0$$

$$\langle \Phi_0 | H_0 | \Psi_0 \rangle^* = \mathcal{E}_0$$

correlation energy

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

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

In FCI $= \langle \Phi_0 | H | \Phi_0 \rangle$

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

$$= \sum_{ai} c_i^a \underbrace{\langle a | f | i \rangle}_{} \langle \Phi_i^a | H | \Phi_0 \rangle$$

$$+ \sum_{\substack{ab \\ ij}} c_{ij}^{ab} \underbrace{\langle ab | v | ij \rangle_{AS}}_{\langle \Phi_{ij}^{ab} | H | \Phi_0 \rangle}$$

Projection operator

$$\hat{P} = | \Phi_0 \rangle \langle \Phi_0 | \quad \Big\{ \text{Model space}$$

$$\hat{P}^2 = \hat{P}$$

$$\hat{P}|\Psi_0\rangle = |\Phi_0\rangle$$

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

$$\hat{P} + \hat{Q} = \mathbb{1}$$

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

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

$$\hat{P}H_0 - H_0\hat{P} = |\Phi_0\rangle\underbrace{\langle\Phi_0|H_0}_{E_0} - H_0|\Phi_0\rangle \langle\Phi_0$$

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

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

$$(\hat{H}_0 + \hat{H}_I)|\Psi_0\rangle = E_0|\Psi_0\rangle$$

adding & subtracting ω

$$(\omega - \hat{H}_0)|\Psi_0\rangle = (\omega - E_0 + \hat{H}_I)|\Psi_0\rangle$$

assume $(\omega - \hat{H}_0)^{-1}$ exists

$$\frac{1}{\omega - \hat{H}_0}$$

$$|\Psi_0\rangle = \frac{1}{\omega - \hat{H}_0}\left[\omega - E_0 + \hat{H}_1\right]|\Psi_0\rangle$$

multiply with $\hat{Q}$ from left

$$\hat{Q}\,\frac{1}{\omega - \hat{H}_0} \qquad [\hat{Q}, \hat{H}_0] = 0$$

$$\hat{Q}^2 = \hat{Q}$$

$$= \frac{\hat{Q}}{\omega - \hat{H}_0} = \hat{Q}\,\frac{1}{\omega - \hat{H}_0}\,\hat{Q}$$

$$= \frac{\sum_{i>1}^{\infty} |\Phi_i\rangle\langle\Phi_i|}{\omega - \hat{H}_0}$$

$$\frac{\hat{Q}}{\omega - \hat{H}_0} |\Psi_0\rangle = \frac{\hat{Q}}{\omega - \hat{H}_0} [\omega - E_0 + H_I] |\Psi_0\rangle$$

$$|\Psi_0\rangle = |\Phi_0\rangle + \frac{\hat{Q}}{\omega - \hat{H}_0} \text{———} \, , \, \text{———} \times |\Psi_0\rangle$$

assume iterative approach,
on r.h.s. we replace $|\Psi_0\rangle_{(0)}$
with $|\Phi_0\rangle$

$$|\Psi_0\rangle_{(1)} \simeq |\Phi_0\rangle + \frac{Q}{\omega - \hat{H}_0} [\omega - E_0 + H_I] |\Phi_0\rangle$$

$$|\Psi_0\rangle_{(2)} = |\Phi_0\rangle +$$

$$\frac{\hat{Q}}{\omega - \hat{H}_0}\left[\omega - E_0 + \hat{H}_1\right]|\Phi_0\rangle$$

$$+ \frac{\hat{Q}}{\omega - \hat{H}_0}\left[\omega - E_0 + \hat{H}_1\right]\frac{\hat{Q}}{\omega - \hat{H}_0}$$

$$\times \left[\omega - E_0 + H_1\right]|\Phi_0\rangle$$

continue til $n = \infty$

$$|\Psi_0\rangle = \sum_{n=0}^{\infty}\left\{\frac{Q}{\omega - \hat{H}_0}(\omega - E_0 + H_1)\right\}^n \times |\Phi_0\rangle$$

multiply with $\langle \Phi_0 | H_1$

$$\langle \Phi_0 | H_1 | u_0 \rangle = \Delta E_0$$

$$= \sum_{n=0}^{\infty} \langle \Phi_0 | H_1 \left\{ \frac{\hat{P}}{\omega - \hat{H}_0} (\omega - E_0 + \hat{H}_1) \right\}^n | \Phi_0$$

Brillouin-Wigner PT

$$\omega = E_0$$

Rayleigh-Schrödinger PT

$$\omega = \mathcal{E}_0$$

Brillouin-Wigner PT

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

$$\sum_{n=0}^{\infty} \langle \Phi_0 | \hat{H}_1 \left\{ \frac{Q}{E_0 - H_0} H_1 \right\}^n | \Phi_0 \rangle$$

1ST

2nd

$$= \langle \Phi_0 | H_1 | \Phi_0 \rangle + \langle \Phi_0 | H_1 \frac{Q}{E_0 - H_0} H_1 | \Phi_0 \rangle$$

$$+ \langle \Phi_0 | H_1 \frac{Q}{E_0 - H_0} H_1 \frac{Q}{E_0 - H_0} H_1 | \Phi_0 \rangle$$

3rd

$$+ \cdots$$

$$\frac{1}{A-B} = \frac{1}{A} + \frac{1}{A} B \frac{1}{A-B}$$

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

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

$$\frac{1}{A-B} = \frac{1}{A} + \frac{1}{A} B \frac{1}{A} + \frac{1}{A} B \frac{1}{A} B \frac{1}{A} + \ldots$$

$$\hat{Q} \frac{1}{e - \hat{Q} H_1 \hat{Q}} \hat{Q} =$$

$$\hat{Q} \left[\frac{1}{e} + \frac{1}{e} Q H_1 Q \frac{1}{e} + \frac{1}{e} Q H_1 Q \frac{1}{e} \right.$$

$$\left. \times Q H_1 Q \frac{1}{e} + \cdots \right] \hat{Q}$$

$$= \frac{\hat{Q}}{e} + \frac{\hat{Q}}{e} H_1 \frac{Q}{e} + \frac{Q}{e} H_1 \frac{Q}{e} H_1 \frac{Q}{e}$$

$$+ \cdots$$

identify $e = E_0 - H_0$

$$\Delta E_0 = \langle \Phi_0 | \hat{H}_1 | \Phi_0 \rangle$$

$$+ \langle \Phi_0 | \hat{H}_1 \hat{Q} \frac{1}{E_0 - \hat{H}_0 - \hat{Q} H_1 Q} \hat{Q} H_1 | \Phi_0 \rangle$$

Back to simple example

$$\overline{\langle \Phi_0 | H | \Phi_0 \rangle} = \underbrace{\varepsilon_1}_{\langle H_0 \rangle} + \underbrace{g}_{\langle H_1 \rangle}$$

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

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

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

$$\underbrace{\langle \Phi_0 | H_1 | \Phi_0 \rangle}_{g} +$$

$$\underbrace{\langle \Phi_0 | H_1 | \Phi_1 \rangle}_{g} \underbrace{\langle \Phi_1 |}_{Q} \frac{1}{E_0 - \varepsilon_2 - \underbrace{\langle \Phi_1 | H_1 | \Phi_1 \rangle}_{g}}$$

$$\times \; | \Phi_1 \rangle \underbrace{\langle \Phi_1 | H_1 | \Phi_0 \rangle}_{g}$$

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

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

$$\det \begin{bmatrix} E_0 - (\varepsilon_1 + g) & g \\ g & E_0 - (\varepsilon_2 + g) \end{bmatrix} = 0$$

RS-PT

$$\omega = \varepsilon_0$$

$$\Delta E_0 = E_0 - \varepsilon_0 =$$

$$\sum_{n=0}^{\infty} \langle \Phi_0 | H_1 \left\{ \frac{Q}{E_0 - H_0} (H_1 - \Delta E_0) \right\}^n$$

$$\left(\Delta E_0 \hat{Q} | \Phi_0 \rangle = 0 \right) \qquad \times | \Phi_0 \rangle$$

$$\Delta E_0 = \langle \Phi_0 | H_1 | \Phi_0 \rangle$$

$$+ \langle \Phi_0 | H_1 \frac{Q}{E_0 - H_0} H_1 | \Phi_0 \rangle$$

$$+ \langle \Phi_0 | H_1 \frac{Q}{E_0 - H_0} (H_1 - \Delta E_0) \frac{Q}{E_0 - H_0} H_1 | \Phi_0$$

$$+ \cdots$$

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

$$\Delta E_0^{(1)} = \langle \Phi_0 | H_1 | \Phi_0 \rangle$$

$$\left(\mathcal{E}_0 + \Delta E_0^{(1)} = E_0^{Ref} \right)$$

$$\Delta E_0^{(2)} = \langle \Phi_0 | H_1 \frac{Q}{\mathcal{E}_0 - H_0} H_1 | \Phi_0 \rangle$$

$$\Delta E_0^{(3)} = \left\langle H_1 \frac{Q}{e_0} H_1 \frac{Q}{e_0} H_1 \right\rangle$$

$$e_0 = E_0 - \hat{H}_0$$

$$- \left\langle H_1 \frac{Q}{e_0} \langle H_1 \rangle \frac{Q}{e_0} H_1 \right\rangle$$

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

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

$$\Delta E_0^{(1)} = \langle \Phi_0 | H_1 | \Phi_0 \rangle$$

$$= \frac{1}{2} \sum_{i'j'} \langle i'j' | v | i'j' \rangle_{AS}$$

$$\Delta E_0^{(2)} = \langle \Phi_0 | \hat{H}_1 \frac{\hat{Q}}{\mathcal{E}_0 - \hat{H}_0} \hat{H}_1 | \Phi_0 \rangle$$

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

$$= \sum_{i=1}^{\infty} \frac{\langle \Phi_0 | H_1 | \Phi_i \rangle \langle \Phi_i | H_1 | \Phi_0 \rangle}{\varepsilon_0 - \varepsilon_i}$$

$$\frac{|\Phi_i\rangle\langle\Phi_i|}{\varepsilon_0 - \hat{H}_0} = \frac{|\Phi_i\rangle\langle\Phi_i|}{\varepsilon_0 - \varepsilon_i}$$

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

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

$$\hat{V}_N = \frac{1}{4} \sum_{pqrs} \langle pq \| v \| rs \rangle a_p^\dagger a_q^\dagger a_s a_r$$

$$\hat{F}_N = \sum_{pq} \langle p | h_0 | q \rangle a_p^\dagger a_q + \sum_{\substack{pq \\ j \le F}} \langle pj | v | qj \rangle_{AS} a_p^\dagger a_q$$

$$\sum_{i=1}^{\infty} |\Phi_i\rangle\langle\Phi_i|$$ can be 1p1h or 2p2h

$$\sum_{ai} \langle \Phi_i^a | \sum_{\substack{pq \\ j}} \langle pj | v | qj \rangle_{AS} \, a_p^\dagger a_q | \Phi_0 \rangle$$

$$a_i^\dagger \, a_a \, a_p^\dagger \, a_q$$

$$= \sum_{\substack{ai \\ j}} \langle aj | v | ij \rangle_{AS}$$

$$\sum_i = \varepsilon_a + \varepsilon_0 - \varepsilon_i$$

$$\varepsilon_0 - \varepsilon_i = \varepsilon_a - \varepsilon_i$$

1p1h intermediate states

$$\Delta E_0^{(2)} = \sum_{aij} \frac{|\langle aj|v|ij\rangle_{AS}|^2}{\varepsilon_i - \varepsilon_a}$$

$$= \sum_{\substack{ai \\ j}} \underbrace{\frac{\langle ij|v|aj\rangle}{\varepsilon_i - \varepsilon_a}}_{\substack{C_i^a(\text{2nd}) \\ \neq C_i^a(\text{FCI})}} \langle aj|v|ij\rangle$$

2p2h

$$\Delta E_0^{(2)} = \sum_{\substack{ab \\ ij}} \frac{\overset{V_{IA}}{\langle ij|v|ab\rangle}\,\overset{V_{AI}}{\langle ab|v|ij\rangle}}{\varepsilon_i+\varepsilon_j-\varepsilon_a-\varepsilon_b}$$

$$C_{ij}^{ab}(\mathrm{MBPT}(2))$$

$$\neq \; C_{ij}^{ab}(\mathrm{FCI})$$